Part A Quantum Theory

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About these notes

These are lecture notes for the Part A Quantum Theory course, which is part of the mathematics syllabus at the University of Oxford. Starred paragraphs are not examinable, typically because they are more difficult and/or slightly off-syllabus. There are two problem sheets for the course, and a revision problem sheet. Please send any questions/corrections/comments to `sparks@maths.ox.ac.uk`.

Reading

- B. H. Bransden and C. J. Joachain, *Quantum Mechanics* (2nd edition, Pearson Education Limited, 2000). Chapters 1–4.

- P. C. W. Davies and D. S. Betts, *Quantum Mechanics (Physics and Its Applications)* (2nd edition, Taylor & Francis Ltd, 1994). Chapters 1, 2, 4.

- R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics, Volume 3* (Addison-Wesley, 1998). Chapters 1, 2 (for physical background).

- K. C. Hannabuss, *An Introduction to Quantum Theory* (Oxford University Press, 1997). Chapters 1–4.

- A. I. M. Rae, *Quantum Mechanics* (4th edition, Taylor & Francis Ltd, 2002). Chapters 1–3.

Preamble

Classical physics – Newton's laws of mechanics and the theory of electromagnetism developed in the 19th century – fails at the atomic scale. From the beginning of the 20th century, mounting experimental evidence pointed towards the existence of a radically different theory of physics that governs the properties of atoms and their constituent particles. The deterministic and continuous nature of classical physics was replaced by a new *quantum theory*, with probability and discreteness at its heart. The theory of quantum mechanics developed in the 20th century not only successfully describes the structure of atoms and molecules, but also nuclear physics, particle physics (such as in particle accelerators like the LHC), chemistry (such as chemical bonding), the structure of solids, superconductors, *etc*. Quantum theory also underpinned many important technological advances in the 20th century, such as the laser, the microchip (hence computers and mobile phones), and the electron microscope. Future applications may include quantum cryptography and the quantum computer.

In this course we begin with an overview of some key physical ideas and formulae. These developed from experiments that demonstrate the failure of classical physics at the atomic scale. An important concept here is *wave-particle duality*. This, together with some intuition from classical physics, will lead us to the *Schrödinger equation* that governs such *matter-waves*. We discuss general properties of the Schrödinger equation, and interpret the wave function in terms of a probability distribution. We also study in detail some of the simplest, and most important, solutions: a particle confined to a box, the harmonic oscillator (which universally describes small oscillations of any quantum system), and finally the hydrogen atom. In particular, we will derive the observed emission/absorption spectrum of the hydrogen atom, a computation that was in Schrödinger's original 1926 paper.

0   Classical particles and waves

Before starting the course proper, we begin with a brief review of classical point particles and waves. This is to remind you of some concepts and formulae learned at school or in Mods, and to set notation used later in the text. A summary of vectors, and in particular differential operators such as $\nabla = \mathbf{grad}$ and the Laplacian ∇^2, is contained in appendix A.

0.1   Point particles

A point particle is an idealized object that, at a given instant of time, is located at a point in space. Considering a time interval $[t_0, t_1] \subset \mathbb{R}$ and modelling space by $\mathbb{R}^3$, the particle's motion is described by $\mathbf{r} : [t_0, t_1] \to \mathbb{R}^3$. This is governed by Newton's second law: if the particle has constant mass m and is acted on by a force $\mathbf{F}$, then $\mathbf{r}(t)$ obeys

$$\mathbf{F} \;\; = \;\; m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} \; . \tag{0.1}$$

In principle here $\mathbf{F} = \mathbf{F}(\mathbf{r}, t)$, although in this course we shall only consider *conservative forces* where $\mathbf{F} = -\nabla V$, for some function $V = V(\mathbf{r})$ called the *potential*. In particular, notice that V is independent of time (*static*). In this case, the total *energy* of the particle

$$E \;\; = \;\; \frac{1}{2}m|\dot{\mathbf{r}}|^2 + V \tag{0.2}$$

is *conserved*, where we shall sometimes denote $\dot{\mathbf{r}} \equiv \mathrm{d}\mathbf{r}/\mathrm{d}t$. That is, E is independent of time:

$$\frac{\mathrm{d}E}{\mathrm{d}t} \;\; = \;\; m\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \cdot \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} + \nabla V \cdot \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \cdot \left(m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} - \mathbf{F} \right) \;\; = \;\; 0 \; . \tag{0.3}$$

Here the particle has *kinetic energy* $\frac{1}{2}m|\dot{\mathbf{r}}|^2$, *potential energy* $V = V(\mathbf{r}(t))$, and *momentum* $\mathbf{p} = m\dot{\mathbf{r}}$. We may also write the kinetic energy as

$$E_{\mathrm{kinetic}} \;\; = \;\; \frac{|\mathbf{p}|^2}{2m} \; . \tag{0.4}$$

A particle that is subjected to no forces is called a *free particle*.

* The above formulae are true (to a very good approximation) for a *non-relativistic* point particle, which means its speed $u = |\dot{\mathbf{r}}|$ is much less than the speed of light, $u \ll c = $ speed of light. For example, a *massless* particle, with $m = 0$, necessarily moves at speed c and has energy $E = c|\mathbf{p}|$, where $\mathbf{p}$ is its momentum (see relativity course next year).

0.2 Waves

Recall the classical *wave equation*

$$\frac{1}{v^2}\frac{\partial^2 \phi}{\partial t^2} = \nabla^2 \phi ,\qquad(0.5)$$

where v is the constant speed of the wave. This linear equation governs, for example, the propagation of sound or light. As basic solution we have the *complex plane wave*

$$\phi(\mathbf{r}, t) = A \exp\left[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] ,\qquad(0.6)$$

where we have the constant *wave vector* $\mathbf{k}$, *angular frequency* ω, and (complex) *amplitude* A. Substituting into (0.5) gives $-\omega^2/v^2 = -|\mathbf{k}|^2$, or equivalently the relation

$$v = \frac{\omega}{|\mathbf{k}|} .\qquad(0.7)$$

Both the real and imaginary parts of ϕ separately satisfy the wave equation, giving real solutions that are linear combinations of sines and cosines in $(\mathbf{k} \cdot \mathbf{r} - \omega t)$. In fact it is a result of Fourier analysis that *every* solution to the wave equation (0.5) is a linear combination (in general involving an integral) of these plane waves.

The *wave frequency* is $\nu = \omega/2\pi$, while the *wavelength* is $\lambda = 2\pi/|\mathbf{k}|$, so that (0.7) is equivalent to saying that the wave speed is $v = \nu\lambda = $ frequency $\times$ wavelength.

1 Physical background and wave-particle duality

1.1 The photoelectric effect and Einstein-Planck relation

In the mid 19th century Maxwell successfully described light as a *wave* propagating in the *electromagnetic field*. We shall not need to know anything about electromagnetic theory in this course. Nevertheless, we note in passing that, in Maxwell's theory, light propagating through a vacuum is described by two vector fields $\mathbf{E}(\mathbf{r}, t)$, $\mathbf{B}(\mathbf{r}, t)$, called the *electric* and *magnetic* fields, respectively, each Cartesian component of which satisfies the wave equation (0.5), with $v = c$ being the speed of light in vacuum. This theory of electromagnetism unified the theories of electricity, magnetism and radiation, and explained wave-like properties of light such as reflection, polarization and diffraction. However, by the beginning of the 20th century it was becoming clear that Maxwell's theory could not explain experiments at the *atomic* scale.

A clear and simple experiment that demonstrates this is the *photoelectric effect*, shown in Figure 1. Light of angular frequency ω is shone on a metal plate in vacuum. Electrons e^-, which are only weakly bound to the metal, are emitted from the surface. One measures their kinetic energy and discovers the formula

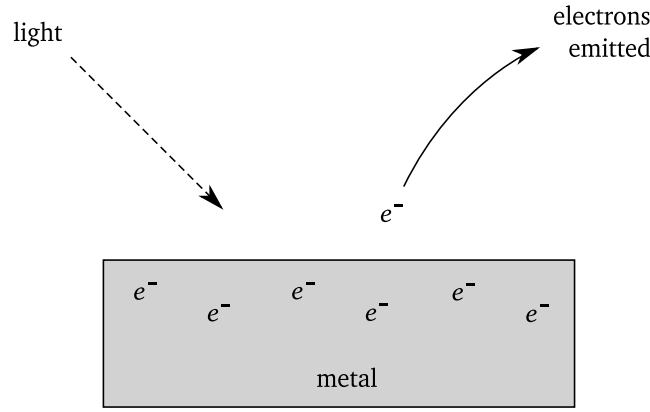$$E_{\text{kinetic}} = -E_0 + \hbar\omega .\qquad(1.1)$$

Figure 1: To observe the photoelectric effect, light is shone on a metal plate in vacuum. Electrons e^- are emitted from the surface of the metal, and their kinetic energy E_{kinetic} is measured.

- $E_0 > 0$ is a constant energy which depends only on the particular metal used.

- The constant of proportionality $\hbar$ (usually read as "h bar") is a constant of Nature that is fundamental to Quantum Theory. From (1.1) we see that it has dimensions $[\hbar] = $ energy $\times$ time, or equivalently $[\hbar] = M(LT^{-1})^2 \times T = MLT^{-1} \times L = $ dimensions of *angular momentum*, where M, L and T denote dimensions of mass, length and time, respectively. Numerically, $\hbar \simeq 1.05 \times 10^{-34}\,\text{J s}$. The combination $2\pi\hbar \equiv h$ is called *Planck's constant*, while $\hbar$ is sometimes referred to as the *reduced Planck's constant*.

- If the angular frequency $\omega < E_0/\hbar$, *no e^- are emitted.*

- The formula (1.1) is independent of the *intensity* (brightness) of the light, but as the latter is increased the *number* of e^- emitted increases.

The classical theory of Maxwell does not explain these observations. Instead Einstein made the following remarkable hypothesis:

Light of angular frequency ω exists in small packets, or "quanta", of energy

$$E \;=\; \hbar\omega \qquad \text{(Einstein-Planck relation)} . \qquad (1.2)$$

These packets of light are known as *photons*, and are massless particles ($m = 0$) that travel at the speed of light c (*cf.* the starred remark at the end of section 0.1). In Einstein's interpretation of the photoelectric effect, each electron e^- absorbs one photon of energy $\hbar\omega$ (very occasionally more than one). Part of this photon energy goes into overcoming the "binding energy" E_0 of the electron to the metal; the remainder is then converted into the observed kinetic energy of e^- when it is emitted. Increasing the intensity of the light simply increases the *number* of photons. Equation (1.2) is called the *Einstein-Planck relation.*[1]

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[1]* Planck had introduced the constant $h = 2\pi\hbar$ in earlier work on radiation emitted from certain idealized hot objects, called *black bodies.*

1.2 Emission/absorption spectra of atoms

Atoms emit and absorb light at very particular frequencies. The simplest atom is the hydrogen atom, which we shall study in more detail at the end of this course. For hydrogen these frequencies were discovered experimentally in the 19th century, and are given by the formula

$$\omega_{n_1,n_2} \;=\; 2\pi R_0 c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \; . \tag{1.3}$$

Here $n_1 < n_2$ are positive *integers*, and $R_0 \simeq 1.10 \times 10^7 \, \mathrm{m}^{-1}$ is *Rydberg's constant*, named after the discoverer of the empirical formula (1.3).

From Einstein's description of light in terms of photons, this implies that a hydrogen atom emits and absorbs photons of particular *energies* $\hbar\omega_{n_1,n_2}$. By conservation of energy, the energy of the hydrogen atom itself must then be changing by these amounts when a photon is emitted/absorbed. This strongly suggests that the energies of the hydrogen atom must be given by

$$E_n \;=\; -\frac{2\pi R_0 \hbar c}{n^2} \; , \tag{1.4}$$

where n is an integer, so that *e.g.* for $n_1 < n_2$ the energy of the atom can change from E_{n_2} to E_{n_1} by emitting a photon of frequency ω_{n_1,n_2}. That the hydrogen atom energies are indeed *quantized* in this way – that is, taking particular discrete values, rather than being continuous – has been confirmed in many other experiments. At the end of this course we will derive (1.4) theoretically.

1.3 The double slit experiment

The photoelectric effect implies that light, described classically by waves satisfying the wave equation (0.5) with speed $v = c$, is sometimes better described as a beam of particles, namely photons.

Similarly, particles, such as the electron e^-, can display wave-like characteristics. Perhaps the best experiment that demonstrates this is the famous *double slit experiment*, performed with electrons. This is shown in Figure 2. A beam of electrons is fired at a double slit configuration, with a detector screen on the other side. An electron hitting the screen appears as a bright spot, and over time one can plot this as a distribution. The latter exhibits a familiar diffraction pattern, similar to that seen in the corresponding experiment with the beam of electrons replaced by a beam of light. Such diffraction patterns are explained by the interference of waves: two waves that travel through each of the slits and arrive at the same point on the detector screen have travelled different distances. These waves then either constructively or destructively interfere with each other, depending on whether the difference in these distances is an even or odd number of wavelengths, respectively. This is perhaps familiar to those who have done A-level physics.

A remarkable point here is that the diffraction pattern is still observed even when only a *single* electron is passing through the slits at a time. In fact this is the case in the Hitachi

(a) Experimental set-up
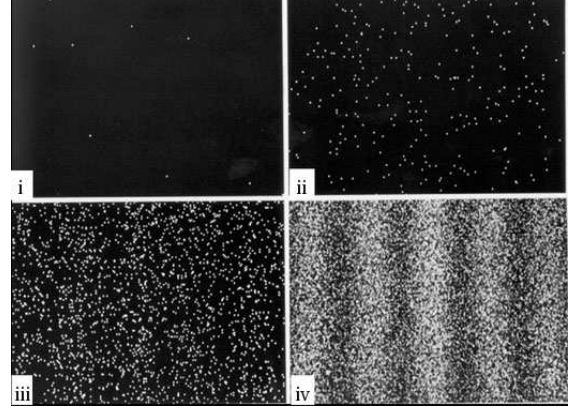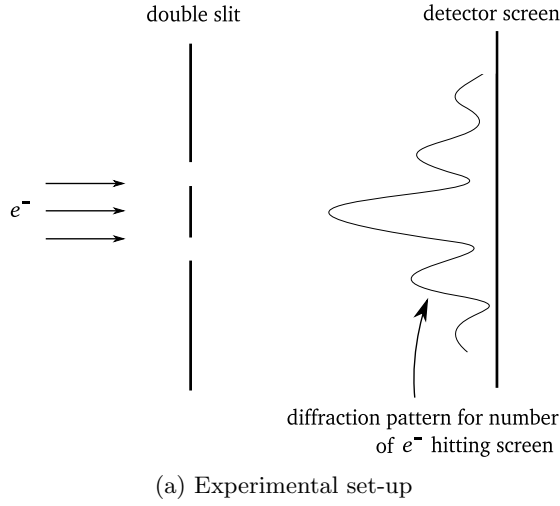
(b) Actual electron hits in an experiment by a group at Hitachi (© Hitachi, Ltd): (i) 8 e^-, (ii) 270 e^-, (iii) 2,000 e^-, (iv) 160,000 e^-.

Figure 2: The double slit experiment, performed with a beam of electrons.

experimental results shown in Figure 2(b) (the time lapse up to picture (iv) is 20 minutes). This implies that the electrons are not interfering with each other to cause the diffraction pattern, but rather a *single* electron is behaving like a wave. Or, more precisely, the detected distribution of electron particles is characteristic of a wave passing between the slits. Notice that we may also interpret this distribution as a *probability distribution* for where any single electron will hit the screen. In this viewpoint, it is the *probability* that displays wave-like characteristics, while the electrons themselves are always detected on the screen as localized particles. These remarks are absolutely central to wave-particle duality.

The double slit experiment (and variants of it) is extremely interesting and subtle, and we refer the interested reader to the references (especially the Feynman lectures) for further discussion of its role in understanding wave-particle duality.

1.4 De Broglie's matter-waves

The experiment we have just described suggests that particles, such as electrons, are also associated with waves. De Broglie made this more precise:

A free particle of energy E and momentum $\mathbf{p}$ is associated with a *wave* of angular frequency ω and wave vector $\mathbf{k}$ via

$$
\begin{aligned}
E &= \hbar\omega \, , \\
\mathbf{p} &= \hbar\mathbf{k} \qquad \text{(de Broglie relations)} \, .
\end{aligned}
\tag{1.5}
$$

Since the wavelength is $\lambda = 2\pi/|\mathbf{k}|$, we may also write the latter relation as $\lambda = 2\pi\hbar/|\mathbf{p}| = h/|\mathbf{p}|$. De Broglie's insight was that these relations should apply to *all* particles, not just massless photons. In this context, $E = \hbar\omega$ is usually referred to as a de Broglie relation, rather than the Einstein-Planck relation.

* We note that for a photon, the second relation in (1.5) is implied by the first relation $E = \hbar\omega$. This follows from the starred comment at the end of section 0.1: for a photon $E = c|\mathbf{p}|$, so that $E = \hbar\omega$ together with $c = \omega/|\mathbf{k}|$ implies that $|\mathbf{p}| = \hbar|\mathbf{k}|$. In Special Relativity, which you can study next year, you'll learn that $(E, \mathbf{p})$ and $(\omega, \mathbf{k})$ are both 4-vectors, and indeed this was part of de Broglie's reasoning.

2 Wave mechanics

2.1 The Schrödinger equation

De Broglie had hypothesized that particles, such as the electron e^-, are associated with waves. Schrödinger set out to discover the equation that governs these *matter-waves*. He began by considering the plane wave, reviewed in section 0.2,

$$\Psi(\mathbf{r}, t) \;=\; A \exp\left[\mathrm{i}(\mathbf{k} \cdot \mathbf{r} - \omega t)\right] \;. \tag{2.1}$$

This of course satisfies the wave equation (0.5), with ϕ replaced by Ψ; the change of notation is meant to emphasize that we now wish to reinterpret this plane wave as a de Broglie matter-wave. Making use of the de Broglie relations (1.5), we notice

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} \;=\; \hbar\omega\Psi \;=\; E\Psi \;,$$
$$-\mathrm{i}\hbar\nabla\Psi \;=\; \hbar\mathbf{k}\Psi \;=\; \mathbf{p}\Psi \;. \tag{2.2}$$

In particular, taking the divergence of the second equation implies that $-\hbar^2\nabla^2\Psi = |\mathbf{p}|^2\Psi$, where ∇^2 is the Laplacian.

The de Broglie relations apply to a free particle, for which the particle's energy is equal to its kinetic energy (since $\mathbf{F} = \mathbf{0}$ the potential is constant, and we take this constant to be zero). If the particle has mass m, then (0.4) relates $E = E_{\text{kinetic}} = |\mathbf{p}|^2/2m$. Using the de Broglie relations (1.5) then implies

$$\omega \;=\; \frac{E}{\hbar} \;=\; \frac{\hbar|\mathbf{k}|^2}{2m} \;. \tag{2.3}$$

Compare this to the relation (0.7). Putting everything together, we have

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} \;=\; E\Psi \;=\; \frac{|\mathbf{p}|^2}{2m}\Psi \;=\; -\frac{\hbar^2}{2m}\nabla^2\Psi \;. \tag{2.4}$$

Thus we may associate to a free particle of mass m a plane wave $\Psi(\mathbf{r}, t)$, using the de Broglie relations, which then satisfies the equation

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} \;=\; -\frac{\hbar^2}{2m}\nabla^2\Psi \;. \tag{2.5}$$

This is essentially expressing the relation (2.3), which is simply the relation between energy and momentum for a free particle.

More generally, a particle of mass m moving in a potential $V = V(\mathbf{r})$ has energy

$$E \;=\; \frac{|\mathbf{p}|^2}{2m} + V \;. \tag{2.6}$$

This led Schrödinger to

Definition / postulate A single, non-relativistic particle of mass m moving in a potential $V(\mathbf{r})$ is described by a *wave function* $\Psi(\mathbf{r}, t)$ that is governed by the *Schrödinger equation*

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \ . \tag{2.7}$$

The wave function $\Psi(\mathbf{r}, t)$ is precisely de Broglie's matter-wave.

Let us make some remarks about what we have done above, which is deceptively straightforward, and about the Schrödinger equation itself:

1. It is important to realize that we have not *derived* the Schrödinger equation, in any rigorous sense. In particular, in the last step we have taken formulae that apply to free particles, that have been suggested by a combination of experiments and theoretical arguments, and extrapolated this, using the classical formula (2.6) for energy, to an equation governing the matter-wave of a particle moving in a general potential. It turns out this equation is indeed correct, but nothing in the rather naive argument we gave really guarantees this. The real test of the Schrödinger equation is that it agrees with experiments.

2. The Schrödinger equation is a *linear* partial differential equation for a *complex-valued* function $\Psi(\mathbf{r}, t)$. Thus if Ψ_1, Ψ_2 are solutions, then so is $\alpha_1\Psi_1 + \alpha_2\Psi_2$, for any complex constants $\alpha_1, \alpha_2 \in \mathbb{C}$. This implies that solutions form a (usually infinite-dimensional) *vector space* over $\mathbb{C}$. It is precisely this superposition of wave functions that leads to interference effects, as in the double slit experiment with electrons. Notice that, in contrast with the classical wave equation (0.5), the Schrödinger equation (2.7) is complex, due to the $i = \sqrt{-1}$ on the left hand side.

3. Although we began our exposition by discussing photons, it is important to remark that the photon is a *massless*, *relativistic* particle, and as such is **not** governed by the Schrödinger equation. The quantum theory of photons is a much more involved theory, known as *quantum electrodynamics*, that requires a thorough understanding of both classical electromagnetism and Special Relativity, as well as quantum ideas. We shall only refer to the photon again in the context of emission/absorption in atoms, for which we need only the Einstein-Planck relation.

Before continuing to discuss some basic mathematical properties of the Schrödinger equation, and looking at our first example, let us pause to comment on the change of viewpoint that is already implicit in what we have said so far. Consider the classical problem of a point particle of mass m moving in a potential V. The dynamics is governed by Newton's law (0.1), with $\mathbf{F} = -\nabla V$, the solutions of which give the particle's trajectory $\mathbf{r}(t)$. For given initial conditions, say the particle's position $\mathbf{r}$ and momentum $\mathbf{p} = m\dot{\mathbf{r}}$ at time $t = t_0$, one solves for the trajectory $\mathbf{r}(t)$, which gives the particle's location and momentum at any subsequent time.

The corresponding quantum mechanical problem is very different. Given a quantum point particle of mass m moving in a potential V, we should instead solve the Schrödinger equation (2.7). We shall discuss the boundary conditions involved later, but notice immediately that the

result will be some complex-valued function $\Psi(\mathbf{r}, t)$. You might immediately wonder what this function has to do with the particle's position at some time t. Again, we shall address this shortly.

2.2 Stationary states

It is natural to seek separable solutions to the Schrödinger equation. Thus we write $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, T(t)$, so that the Schrödinger equation (2.7) becomes

$$\frac{i\hbar \frac{dT}{dt}}{T} = \frac{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi}{\psi} \ . \tag{2.8}$$

Since the left hand side depends only on t, while the right hand side depends only on $\mathbf{r}$, both sides must be constant. If we call this constant E (anticipating that this will be the energy of the particle), then in particular we have

$$i\hbar\frac{dT}{dt} = ET \ , \tag{2.9}$$

which immediately integrates to

$$T(t) = e^{-iEt/\hbar} \ . \tag{2.10}$$

Here we have absorbed the overall multiplicative integration constant into ψ. The full wave function is thus

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iEt/\hbar} \ . \tag{2.11}$$

That E is then indeed the energy of the particle follows from the de Broglie relation between energy and angular frequency for matter-waves: for this wave function the angular frequency is $\omega = E/\hbar$, or equivalently $E = \hbar\omega$. The function ψ then satisfies

Definition The *time-independent*, or *stationary state*, *Schrödinger equation* for a particle of mass m and energy E moving in a potential $V = V(\mathbf{r})$ is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \ . \tag{2.12}$$

The wave function $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iEt/\hbar}$ is then called a *stationary state wave function* of energy E, although in a common abuse of language the function ψ is also often referred to as the stationary state wave function.

2.3 One-dimensional equations

Although ultimately we are interested in studying particles moving in the three spatial dimensions that we observe, it is often technically more straightforward to study the *one-dimensional Schrödinger equation*

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \ , \tag{2.13}$$

with corresponding stationary state equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi \;\; = \;\; E\psi \;, \tag{2.14}$$

and

$$\Psi(x,t) \;\; = \;\; \psi(x)\,\mathrm{e}^{-\mathrm{i}Et/\hbar}\;. \tag{2.15}$$

Here we have replaced the Laplacian ∇^2 by the corresponding one-dimensional operator, which is simply $\partial^2/\partial x^2$ (see appendix A). Equations (2.13), (2.14) govern a particle propagating on the x-axis with potential $V = V(x)$. Similar remarks apply in two dimensions. Although the one-dimensional equation looks somewhat unphysical, in fact sometimes a three-dimensional problem effectively reduces to a lower-dimensional Schrödinger equation; for example, due to symmetry reduction (see section 5), or because the particle is constrained to lie in some subspace.

2.4 Particle in a box

Consider a particle inside a "box" on the x-axis. This means that the particle moves freely inside some interval $[0, a] \subset \mathbb{R}$, but cannot leave this region. One can model this by a potential function $V = V(x)$ that is zero inside the interval/box, and infinite outside:

$$V(x) \;\; = \;\; \begin{cases} 0\;, & 0 < x < a\;, \\ +\infty\;, & \text{otherwise}\;. \end{cases} \tag{2.16}$$

This is also sometimes referred to as the *infinite square well potential*. See Figure 3.
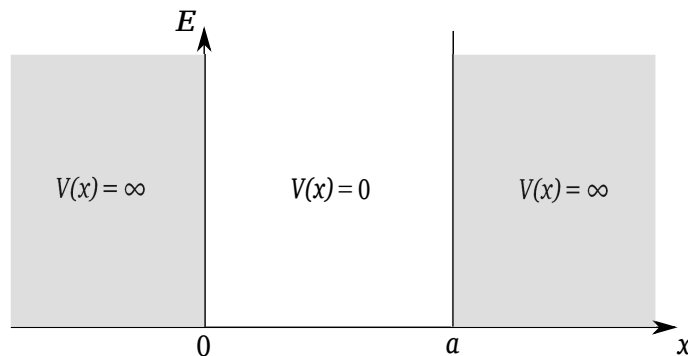

Figure 3: A particle in box $[0, a]$ on the x-axis.

Before discussing the quantum problem, let us briefly comment on the classical problem. Since $V = 0$ inside the box, the classical particle moves at some constant velocity, or equivalently constant momentum p. Since the energy $E = p^2/2m$ is conserved when the particle hits the edge of the box, after the collision p is replaced by $-p$ and the particle heads towards the other edge of the box. Classically, notice that E may take any non-negative value.

Now let us consider the quantum particle. The stationary state Schrödinger equation (2.14) *inside the box* is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \;\; = \;\; -\frac{2mE}{\hbar^2}\psi\;, \tag{2.17}$$

10

for $x \in (0, a)$. We shall discuss boundary conditions more systematically in section 3.2, but here we note that since $V = \infty$ outside the box, the Schrödinger equation will make sense only if $\psi = 0$ there.[2] When we come to discuss the physical meaning of the wave function, we shall see that this assertion is very well justified physically. If we also assume that ψ is *continuous*, then we must solve (2.17) subject to the *boundary condition* $\psi(0) = \psi(a) = 0$.

The general solution to (2.17) is

$$
\psi(x) = \begin{cases} A \cos \frac{\sqrt{2mE}}{\hbar} x + B \sin \frac{\sqrt{2mE}}{\hbar} x , & E > 0 , \\ A + Bx , & E = 0 , \\ A \cosh \frac{\sqrt{-2mE}}{\hbar} x + B \sinh \frac{\sqrt{-2mE}}{\hbar} x , & E < 0 . \end{cases} \tag{2.18}
$$

In all cases the boundary condition $\psi(0) = 0$ implies $A = 0$. When $E \leq 0$, $\psi(a) = 0$ implies also $B = 0$. Thus the only solution is $\psi \equiv 0$, which is always a physically meaningless solution to the Schrödinger equation (again, we shall discuss this more later). On the other hand, for $E > 0$ the boundary condition $\psi(a) = 0$ implies that (either $B = 0$ and $\psi \equiv 0$ or)

$$
\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} , \tag{2.19}
$$

for some *integer* $n \in \mathbb{Z}$. Thus the solutions

$$
\psi(x) = \psi_n(x) = \begin{cases} B \sin \frac{n\pi x}{a} , & 0 < x < a , \\ 0 , & \text{otherwise} , \end{cases} \tag{2.20}
$$

are labelled by n. Notice that, without loss of generality, we may take $n > 0$. The first three wave functions, for $n = 1, 2, 3$, are shown in Figure 4.
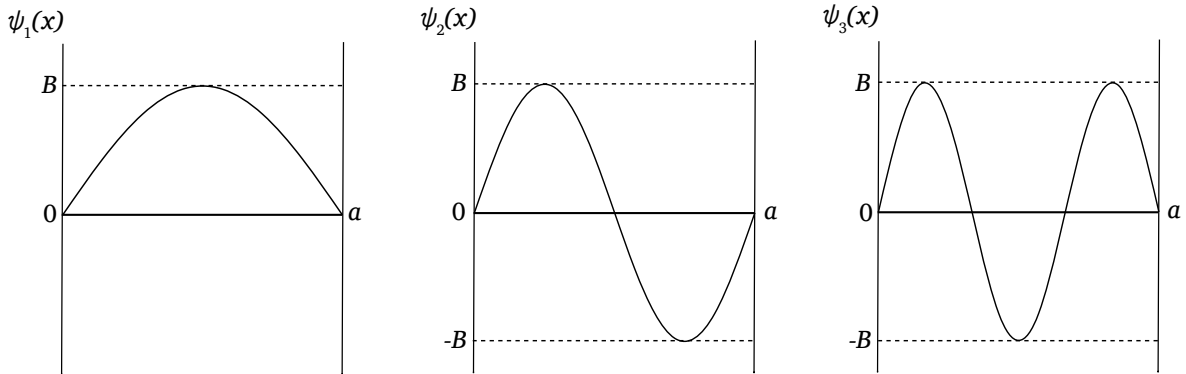

Figure 4: Wave functions for the first three states of a particle in a box. $\psi_1(x)$ is the ground state wave function.

The associated energies are, from (2.19),

$$
E = E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} . \tag{2.21}
$$

We see immediately that the energy is *quantized*, *i.e.* it takes values in a discrete set, here labelled by a positive integer. This is in stark contrast with the energy of the classical particle,

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[2]This is not a very rigorous statement. We can make the discussion rigorous by simply declaring that a particle in a box by definition has $\psi = 0$ outside the box and that ψ is everywhere continuous. See also section 3.2.

which may take any real non-negative value. There is also a lowest energy, given by setting $n = 1$.

Definition When the possible energies of a quantum system are discrete and bounded below, the lowest possible energy is called the *ground state energy* (also sometimes called the *zero point energy*). The higher energies are, in increasing order, the *first excited state energy*, *second excited state energy, etc.* The corresponding wave functions are called the *ground state wave function*, kth *excited state wave function.*

For the particle in a box the ground state energy is $E_1 = \pi^2 \hbar^2 / 2ma^2$, while $E_n = n^2 E_1$. Of course, we precisely wanted a theoretical understanding of such quantized energies in order to explain the energy levels of the hydrogen atom, determined empirically as (1.4). For the particle in a box, if we take $m = m_{e^-} \simeq 9.11 \times 10^{-31}$ kg to be the mass of an electron and $a = 10^{-10}$ m to be the approximate size of an atom, we obtain

$$E_n \quad \simeq \quad 5.97 \times 10^{-18} \, n^2 \text{ J} . \tag{2.22}$$

In particular, the difference in energies between the ground state and first excited state is $E_2 - E_1 \simeq 1.79 \times 10^{-17}$ J. A photon that is emitted in a transition between these energy levels then has a wavelength $\lambda \simeq 1.12 \times 10^{-8}$ m (on the boundary between the ultraviolet and X-ray parts of the electromagnetic spectrum), which is indeed the correct order of magnitude observed in atomic transitions! Here we are effectively modelling a hydrogen atom as an electron confined to an atom-sized box, which is very crude; we shall treat the hydrogen atom more precisely in section 5. Nevertheless, the above computation is encouraging.

The full time-dependent wave functions (2.15) are

$$\Psi_n(x, t) \quad = \quad \begin{cases} B \sin \frac{n\pi x}{a} \, \mathrm{e}^{-\mathrm{i}n^2 \pi^2 \hbar t / 2ma^2} , & 0 < x < a , \\ 0 , & \text{otherwise} . \end{cases} \tag{2.23}$$

Any linear combination of such wave functions satisfies the time-dependent Schrödinger equation (2.13); in particular, the space of solutions, or possible wave functions, is *infinite dimensional.*

In this example the energy levels E_n, and associated stationary state wave functions ψ_n, are labelled naturally by a (positive) integer n. As we shall see throughout the course, such integers arise in many important solutions to the Schrödinger equation, and they are generally known as *quantum numbers* (although it is difficult to give a precise general definition).

2.5 Degeneracy

Having studied a particle in a one-dimensional box, it is now straightforward to extend this to a three-dimensional box.

Consider a particle confined to the box region given by $\{(x, y, z) \in \mathbb{R}^3 \mid 0 \leq x \leq a, 0 \leq y \leq b, 0 \leq z \leq c\} \subset \mathbb{R}^3$, where the potential is zero inside the box. In other words,

$$V(x, y, z) \quad = \quad \begin{cases} 0 , & 0 < x < a, \ 0 < y < b, \ 0 < z < c , \\ +\infty , & \text{otherwise} . \end{cases} \tag{2.24}$$

As before, the stationary state wave function $\psi(\mathbf{r}) = \psi(x, y, z)$ is taken to be zero on, and outside, the boundary of the box region. Inside the box the stationary state Schrödinger equation (2.12) reduces to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{2mE}{\hbar^2}\psi \ . \tag{2.25}$$

This may be solved by separation of variables. Equation (2.25) essentially reduces to three copies of the one-dimensional equation, with the wave functions labelled by three quantum numbers $n_1, n_2, n_3 \in \mathbb{Z}_{>0}$. Explicitly, inside the box these are given by

$$\psi_{n_1,n_2,n_3}(x, y, z) = B \sin\frac{n_1\pi x}{a} \sin\frac{n_2\pi y}{b} \sin\frac{n_3\pi z}{c} \ , \tag{2.26}$$

with B again an arbitrary constant, and the corresponding energies are

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right) \ . \tag{2.27}$$

Exercise (Problem Sheet 1) Derive the wave functions (2.26) and energies (2.27) by solving (2.25) by separation of variables.

Definition If the space of solutions to the stationary state Schrödinger equation with energy E has dimension $d > 1$, we say this energy level is *d-fold degenerate*; if it is one-dimensional we say E is a *non-degenerate* energy level.

For the one-dimensional particle in a box all the energy levels are non-degenerate. However, consider now the three-dimensional box with equal length sides $a = b = c$, so that

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_1^2 + n_2^2 + n_3^2\right) \ . \tag{2.28}$$

In this case there are *linearly independent* wave functions with the *same* energy. For example, we may take (n_1, n_2, n_3) to be any of $(2, 1, 1)$, $(1, 2, 1)$, $(1, 1, 2)$, all of which have the *same* energy $E = 6\pi^2\hbar^2/2ma^2$. There is thus a three-fold degeneracy in the number of quantum stationary states with this energy. The degeneracy in this case is related to the *symmetry* of the potential. We shall see other examples of this later.

3 The Born interpretation

We have now met the Schrödinger equation and solved it in the simplest interesting example, namely a particle confined to a box. We have seen that this leads to quantized energy levels, and that by crudely modelling a hydrogen atom as an electron confined to an atom-sized box, we obtain energies of the correct order of magnitude seen in atomic transitions.

An immediate question is: *what is the physical meaning of the wave function $\Psi(\mathbf{r}, t)$ that we are solving for?* Comparing to the corresponding classical problem, described at the end of section 2.1, we may also ask: where is the particle at time t? In this section we shall answer these questions.

3.1 Probability density

In order to motivate the interpretation that follows, we begin by going back to the double slit experiment in section 1.3. In fact let us begin by discussing the corresponding experiment with light (also called *Young's experiment*). In this case the *intensity* of the light hitting the detector screen forms an interference pattern, and in classical electromagnetic theory this intensity is proportional to the *absolute value squared of the amplitude of the wave*. Unfortunately we won't have time to explain this in detail here, but this fact would have been well-known to the pioneers of quantum theory in the early 20th century. In the double slit experiment with electrons, we instead plot the spatial distribution of electrons hitting the detector screen over some long period of time, and then reinterpret this as a *probability distribution* for where any given electron will hit the screen.

If we now conflate these observations, we are led to the hypothesis that the *probability density function* for an electron hitting the detector screen is given by the *absolute value squared of the de Broglie wave* associated to the electron. Of course, the detector screen could be anywhere, and the de Broglie wave is precisely the wave function $\Psi(\mathbf{r}, t)$ appearing in the Schrödinger equation. Hence we arrive at:

Definition / postulate The function

$$\rho(\mathbf{r}, t) \;\; \equiv \;\; |\Psi(\mathbf{r}, t)|^2 \; , \tag{3.1}$$

is a *probability density function* for the position of the particle, where $\Psi(\mathbf{r}, t)$ is the particle's wave function.

This interpretation of Schrödinger's wave function is due to Born.

The assertion (3.1) is equivalent to the statement that the probability of finding the particle in a volume $D \subset \mathbb{R}^3$ is given by

$$P_\Psi(D) \;\; = \;\; \int_D |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \; . \tag{3.2}$$

This probability depends both on the region D, and also on the wave function $\Psi(\mathbf{r}, t)$ satisfying the Schrödinger equation. We have already seen for the particle in a box that the space of solutions to the Schrödinger equation is an infinite-dimensional vector space, with basis (2.23). A given solution is said to describe the *state* of the particle, so that the probabilities (3.2) depend on the state. Notice $P_\Psi(D)$ also depends in general on time t, although this is suppressed in the notation.

Of course, the above assertions immediately raise some issues. In particular, the probability of finding the particle *somewhere* in $\mathbb{R}^3$ should equal 1, at any time. Thus for (3.1), or equivalently (3.2), to make sense, the wave function must be *normalized* in the following sense:

Definition A wave function Ψ is said to be *normalizable* if

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \;\; < \;\; \infty \; , \qquad \forall \text{ time } t \; . \tag{3.3}$$

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Moreover, if

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x \;\; = \;\; 1 \;, \qquad \forall \text{ time } t \;, \tag{3.4}$$

then Ψ is said to be a *normalized wave function*.

Similar definitions apply in one dimension. For example, the normalized condition (3.4) becomes

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 \, \mathrm{d}x \;\; = \;\; 1 \;. \tag{3.5}$$

Let us make some remarks:

1. The normalized condition (3.4) fixes the freedom to multiply a given solution to the Schrödinger equation by a complex constant, up to a constant *phase* $\mathrm{e}^{\mathrm{i}\varphi}$. The latter is in fact not physical, so that wave functions differing by a constant phase are physically equivalent. Notice also that the normalized condition rules out the *trivial solution* $\Psi \equiv 0$.

2. For the particle in a box, the wave functions (2.23) are normalizable:

$$\int_{-\infty}^{\infty} |\Psi_n(x, t)|^2 \, \mathrm{d}x \;\; = \;\; |B|^2 \int_0^a \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x \;\; = \;\; \frac{1}{2} a |B|^2 \;. \tag{3.6}$$

The total wave functions

$$\Psi_n(x, t) \;\; = \;\; \begin{cases} \sqrt{\frac{2}{a}} \, \sin \frac{n\pi x}{a} \, \mathrm{e}^{-\mathrm{i}n^2\pi^2 \hbar t / 2ma^2} \;, & 0 < x < a \;, \\ 0 \;, & \text{otherwise} \;, \end{cases} \tag{3.7}$$

with $B = \sqrt{2/a}$, are then *normalized*. Note that a particle being "confined to a box" may be interpreted as saying that there is *zero probability* of finding it anywhere outside the box, or in other words that the wave function is identically zero outside the box.

3. More generally, notice that for a stationary state of energy E, we have

$$\rho(\mathbf{r}, t) \;\; = \;\; |\Psi(\mathbf{r}, t)|^2 \;\; = \;\; \left| \psi(\mathbf{r}) \, \mathrm{e}^{-\mathrm{i}Et/\hbar} \right|^2 \;\; = \;\; |\psi(\mathbf{r})|^2 \;. \tag{3.8}$$

Thus $\Psi(\mathbf{r}, t)$ is normalized for all time provided $\psi(\mathbf{r})$ is normalized, *i.e.*

$$\int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2 \, \mathrm{d}^3 x \;\; = \;\; 1 \;. \tag{3.9}$$

4. Recall that the plane wave

$$\Psi(\mathbf{r}, t) \;\; = \;\; A \exp\left[\mathrm{i} \left(\mathbf{k} \cdot \mathbf{r} - \frac{\hbar |\mathbf{k}|^2 t}{2m} \right) \right] \;, \tag{3.10}$$

satifies the free Schrödinger equation ($V = 0$), and was interpreted as describing a free particle of mass m and momentum $\mathbf{p} = \hbar \mathbf{k}$ – see the discussion around equation (2.3). However, clearly $|\Psi(\mathbf{r}, t)|^2 = |A|^2$ is not integrable over $\mathbb{R}^3$, and thus the plane wave is *not* normalizable! In fact the plane wave is better interpreted as a *beam* of particles of mass m and momentum $\mathbf{p}$.

* Some further, off-the-record, comments are in order about the plane wave. The plane wave is typically used in quantum mechanics in *scattering problems*. Here it is interpreted as an incoming beam of free particles of mass m and momentum $\mathbf{p} = \hbar\mathbf{k}$, which then scatter off some potential V that is non-constant only in a localized region of space. Readers who would like to learn more about this topic, which is elementary but beyond our syllabus, might like to read Chapter 5 of the book by Hannabuss.

Alternatively, one can construct a localized *(Gaussian) wave packet* by taking an appropriate linear combination of plane waves. More precisely, this linear combination is realized as an integral over $\mathbf{k}$. The resulting wave function satisfies the free Schrödinger equation and is *normalized*, although the wave packet spreads out as time increases. Again, we refer the interested reader to the references, rather than being more precise here.

Finally, the real physical reason why the plane wave is not normalizable is because it describes a particle of *definite momentum*. In quantum theory one cannot simultaneously know the precise position and momentum of any particle, a fact known as Heisenberg's Uncertainty Principle; the more precisely one knows one quantity, the less precisely one knows the other. Since the plane wave particle has definite momentum, its position is completely uncertain, which explains why its formal probability density is a constant – it is equally likely be found *anywhere* in space. This fascinating implication of quantum mechanics is not something we will have time to explore in this course. This starred section is in any case getting ahead of ourselves, and the reader should perhaps ignore the above comments on a first reading, or indeed ignore them altogether if they are confusing.

Example (Particle in a box) Let us apply the above ideas to the particle in a one-dimensional box. The normalized wave functions are (3.7). The corresponding probability density functions are then, for $x \in [0, a]$, given by

$$\rho_n(x) \;\; = \;\; \frac{2}{a}\sin^2\frac{n\pi x}{a} \;\; = \;\; \frac{1}{a}\left(1 - \cos\frac{2n\pi x}{a}\right) \;, \tag{3.11}$$

and identically zero outside the box. Plots of the probability density functions for the ground state and first two excited states are shown in Figure 5.
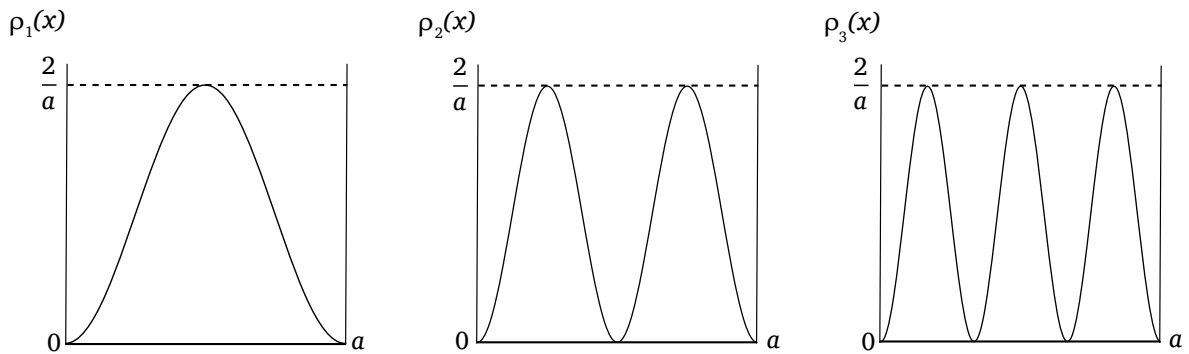

Figure 5: Probability density functions for the first three states of a particle in a box.

As usual in probability theory, we may define the *distribution function* as

$$F_n(x) \;\; \equiv \;\; \int_0^x \rho_n(y)\,\mathrm{d}y \;\; = \;\; \frac{x}{a} - \frac{1}{2n\pi}\sin\frac{2n\pi x}{a} \;. \tag{3.12}$$

Notice in particular that the first term, $\frac{x}{a}$, is the result for the *uniform distribution*, where the particle is equally likely to be found anywhere in $[0, a]$. This is interpreted as the *classical result*.

By this we mean that if we are ignorant of the state of the classical particle before we observe its position, then because it moves at constant velocity back and forth across the box, it is equally likely to be found anywhere. The second, oscillatory term in (3.12) is then a *quantum contribution*, or *quantum correction*, to the classical result.

Let us compute some example probabilities using these formulae. The probability that the particle is within $\frac{a}{4}$ distance from the centre of the box is given by

$$
\begin{aligned}
\int_{\frac{a}{4}}^{\frac{3a}{4}} |\psi_n(x)|^2 \, \mathrm{d}x &= F_n\left(\frac{3a}{4}\right) - F_n\left(\frac{a}{4}\right) , \\
&= \frac{1}{2} + \frac{1}{n\pi} \sin \frac{n\pi}{2} , \\
&= \begin{cases} \frac{1}{2} , & n \text{ even} , \\ \frac{1}{2} + \frac{(-1)^{(n-1)/2}}{n\pi} , & n \text{ odd} . \end{cases}
\end{aligned}
\tag{3.13}
$$

In particular, we see that this *approaches the classical result* of $\frac{1}{2}$, for the uniform distribution, as $n \to \infty$. The tendancy of quantum results to approach those of the corresponding classical theory for large quantum numbers is called the *correspondence principle*.

We may similarly use the probability density ρ to compute *expectation values*:

Definition In quantum mechanics the *expectation value of a function of position $f(\mathbf{r})$* is denoted

$$
\langle f(\mathbf{r}) \rangle_\Psi \equiv \int_{\mathbb{R}^3} f(\mathbf{r}) \, |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3 x .
\tag{3.14}
$$

The reason for the strange brackets on the left hand side will become apparent if you study quantum mechanics in the third year. Notice that again this expectation value depends on the wave function/state Ψ, and in general is a function of time t.

Example For the particle in a box we compute the expected value of its position

$$
\begin{aligned}
\langle x \rangle_{\Psi_n} &= \int_0^a x \, \rho_n(x) \, \mathrm{d}x , \\
&= [x \, F_n(x)]_0^a - \int_0^a F_n(x) \, \mathrm{d}x , \\
&= a - \left[\frac{x^2}{2a} + \frac{a}{4n^2\pi^2} \cos \frac{2n\pi x}{a} \right]_0^a , \\
&= \frac{1}{2}a ,
\end{aligned}
\tag{3.15}
$$

agreeing with the classical result for the uniform distribution.

3.2   The continuity equation and boundary conditions

In this section we consider more carefully the *boundary conditions* involved in the Schrödinger equation.

Proposition 3.1 *The Schrödinger equation implies the* continuity equation

$$
\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 ,
\tag{3.16}
$$

where $\rho(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$ is the probability density we have already met, and the vector field

$$\mathbf{j}(\mathbf{r}, t) \equiv \frac{i\hbar}{2m} \left(\Psi(\mathbf{r}, t)\overline{(\nabla\Psi)(\mathbf{r}, t)} - \overline{\Psi(\mathbf{r}, t)}(\nabla\Psi)(\mathbf{r}, t) \right) , \tag{3.17}$$

is the probability current $\mathbf{j}$.

Proof This is a direct computation:

$$
\begin{aligned}
\frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)|^2 &= \left(\frac{\partial}{\partial t}\overline{\Psi(\mathbf{r}, t)} \right) \Psi(\mathbf{r}, t) + \overline{\Psi(\mathbf{r}, t)}\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) , \\
&= \overline{\left[-\frac{i}{\hbar} \left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \right) \right]}\Psi + \overline{\Psi}\left[-\frac{i}{\hbar} \left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \right) \right], \text{(Schrödinger)} \\
&= \frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\overline{\Psi} + V\overline{\Psi} \right)\Psi - \overline{\Psi}\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \right) , \quad (V \text{ is real}) \\
&= \frac{i\hbar}{2m}\left(\overline{\Psi}\,\nabla^2\Psi - \Psi\,\nabla^2\overline{\Psi} \right) , \\
&= \frac{i\hbar}{2m}\nabla \cdot \left(\overline{\Psi}\,\nabla\Psi - \Psi\,\nabla\overline{\Psi} \right) = -\nabla\cdot\mathbf{j} . \quad \blacksquare \tag{3.18}
\end{aligned}
$$

This leads to the following result:

Proposition 3.2 *Suppose that $\forall$ time t, $\mathbf{j}(\mathbf{r}, t)$ satisfies the boundary condition that it tends to zero faster than $1/|\mathbf{r}|^2$ as $|\mathbf{r}| = r \to \infty$. Then*

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3x \tag{3.19}$$

is independent of t. In particular, if Ψ is normalized at some time $t = t_*$, it is normalized $\forall t$.

Proof Let S be a closed surface that encloses a region $D \subset \mathbb{R}^3$. Then

$$
\begin{aligned}
\frac{\partial}{\partial t}\int_D |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3x &= \int_D \frac{\partial\rho}{\partial t} \, \mathrm{d}^3x , \quad \text{(derivative through the integral)} \\
&= \int_D (-\nabla\cdot\mathbf{j}) \, \mathrm{d}^3x , \quad \text{(continuity equation)} \\
&= -\int_S \mathbf{j}\cdot\mathrm{d}\mathbf{S} , \quad \text{(Divergence Theorem)} . \tag{3.20}
\end{aligned}
$$

We refer the reader to appendix A for a reminder of the Divergence Theorem. In particular, $\mathrm{d}\mathbf{S} = \mathbf{n}\,\mathrm{d}S$ where $\mathrm{d}S$ is the area element of S and $\mathbf{n}$ is the outward pointing unit normal vector to S.

Now take S to be a sphere of radius $r > 0$, centred on the origin, so that D is a ball. Then $\mathbf{n} = \dfrac{\mathbf{r}}{r}$ and hence

$$\mathbf{j}\cdot\mathrm{d}\mathbf{S} = \mathbf{j}\cdot\mathbf{n}\,r^2\,\mathrm{d}S_{\text{unit}} , \tag{3.21}$$

where $\mathrm{d}S_{\text{unit}}$ is the area element on a *unit* radius sphere. In general, the function $\mathbf{j}\cdot\mathbf{n}$ will depend on r and the angular variables θ, ϕ on the sphere (and on time t). Provided $\mathbf{j}\cdot\mathbf{n} = o(1/r^2)$, uniformly in the angular coordinates, then using (3.21) the surface integral in (3.20) tends to zero as $r \to \infty$, and hence

$$\frac{\partial}{\partial t}\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3x = 0 , \tag{3.22}$$

which implies that the expression in (3.19) is independent of t. $\quad\blacksquare$

We now state more formally the conditions that solutions to the Schrödinger equation should satisfy:

1. *The wave function $\Psi(\mathbf{r}, t)$ should be a continuous, single-valued function.* This condition ensures that the probability density $\rho = |\Psi|^2$ is single-valued and has no discontinuities. We already imposed the continuity property for the particle in a box.

2. *Ψ should be normalizable, i.e. the integral of $|\Psi|^2$ over all space should be finite.* Proposition 3.2 ensures that if the probability current $\mathbf{j}$ in (3.17) tends to zero fast enough at infinity, then this integral is independent of time t. Then if Ψ is normalizable, we may normalize it for all time. Without this condition, the probabilistic interpretation of the wave function is not possible. As already mentioned, this condition may be relaxed for free particles and scattering problems, although we shall not consider such wave functions any further in this course.

3. *$\nabla\Psi$ should be continuous everywhere, except where there is an infinite discontinuity in the potential V.* This condition follows since a finite discontinuity in $\nabla\Psi$ implies an infinite discontinuity in $\nabla^2\Psi$, and thus from the Schrödinger equation an infinite discontinuity in V. Again, we encountered precisely this behaviour for the particle in a box.

3.3 Measurement of energy

In section 2.2 we found separable solutions to the time-dependent Schrödinger equation (2.7). The corresponding stationary states (2.11) have definite frequency, and hence definite energy E. For example, the complete set of stationary state wave functions for a particle in a box is given by (3.7). Since the time-dependent Schrödinger equation is *linear*, any linear combination of such stationary state wave functions also solves the Schrödinger equation. Thus we may in general write

$$\Psi(\mathbf{r}, t) \;\; = \;\; \sum_n \alpha_n\, \psi_n(\mathbf{r})\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar}\;, \tag{3.23}$$

where n labels some set of stationary states $\psi_n(\mathbf{r})$ of energy E_n, and $\alpha_n \in \mathbb{C}$ are constants.

For the particle in a box, (3.23) is simply a *Fourier sine series*. From Mods you know that any sufficiently well-behaved[3] function $f : [0, a] \to \mathbb{C}$ with $f(0) = f(a) = 0$ can be expanded as a Fourier sine series

$$f(x) \;\; = \;\; \sum_{n=1}^{\infty} \alpha_n \sqrt{\frac{2}{a}}\, \sin\frac{n\pi x}{a} \;\; = \;\; \sum_{n=1}^{\infty} \alpha_n\, \psi_n(x)\;, \tag{3.24}$$

for appropriate α_n. Then given *any* such function $f(x)$, we obtain a corresponding solution to the time-dependent Schrödinger equation using (3.23):

$$\Psi(x, t) \;\; = \;\; \sum_{n=1}^{\infty} \alpha_n\, \psi_n(x)\, \mathrm{e}^{-\mathrm{i}E_n t/\hbar}\;, \tag{3.25}$$

---

[3]* For the application to wave functions below, we require the wave function to be *normalizable* as in (3.3). For the particle in a box example, this implies that $\int_0^a |f(x)|^2 \,\mathrm{d}x < \infty$. In fact this is then sufficient for the Fourier series (3.24) to converge almost everywhere to $f(x)$.

where the coefficients α_n are determined via (3.24), and for the particle in a box the energies E_n are given by (2.21). We have thus solved the initial value problem for the Schrödinger equation, with $\Psi(x, t = 0) = f(x)$. Note that the normalized stationary state wave functions $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ are also orthonormal

$$\int_0^a \psi_m(x)\, \psi_n(x)\, \mathrm{d}x \quad = \quad \delta_{mn} \ . \tag{3.26}$$

Definition / interpretation Suppose that the *normalized* wave function for a particle in a box is given by (3.25). Then the *probability* of measuring the energy of the particle to be E_n is $|\alpha_n|^2$.

This definition makes sense, since

$$1 \;=\; \int_0^a |\Psi(x, t)|^2 \, \mathrm{d}x \;=\; \sum_{m,n=1}^{\infty} \overline{\alpha}_m\, \alpha_n\, \mathrm{e}^{-\mathrm{i}(E_n - E_m)t/\hbar} \int_0^a \overline{\psi}_m(x)\, \psi_n(x)\, \mathrm{d}x \;=\; \sum_{n=1}^{\infty} |\alpha_n|^2 \ . \tag{3.27}$$

Notice that if the particle's wave function is a stationary state of energy E_n, then the probability of measuring the particle's energy to be E_n is 1. It thus makes sense to say that a stationary state (2.11) describes a particle of *definite energy E*.

In fact the expansion (3.23) of any wave function $\Psi(\mathbf{r}, t)$ exists under very general conditions, *i.e.* for general choices of potential $V(\mathbf{r})$, and generalizes to cases with degenerate energy levels or even a continuous energy spectrum. We have only discussed the quantum probabilistic interpretation of position and energy in this course, and our treatment of these two *observables* looks rather different. However, there is an elegant unified description of position and energy measurement that extends to *all* observables in quantum mechanics (including in particular momentum). This is described in the course B7.1a.

4 The harmonic oscillator

The quantum harmonic oscillator is ubiquitous in physics, and as such is probably the most important solution to the Schrödinger equation.

4.1 The one-dimensional harmonic oscillator

Consider a particle of mass m moving in one dimension under the influence of a potential $V(x)$. Near to a critical point x_0 of V, where $V'(x_0) = 0$, we have the Taylor expansion

$$V(x) \quad = \quad V(x_0) + \tfrac{1}{2} V''(x_0)(x - x_0)^2 + O\left((x - x_0)^3\right) \ . \tag{4.1}$$

If $V''(x_0) > 0$ then x_0 is a *local minimum* of the potential. Without loss of generality let us choose coordinates where the critical point x_0 is at the origin. Then to lowest order the potential near to $x_0 = 0$ is

$$V(x) \quad = \quad V(0) + \frac{1}{2} m\omega^2 x^2 \ , \tag{4.2}$$

where we have defined $\omega^2 = V''(0)/m$. The dynamics is not affected by the value of $V(0)$, since an additive constant drops out of the force $F = -V'$. The *harmonic oscillator potential* is

$$V(x) = \frac{1}{2}m\omega^2 x^2 \ . \tag{4.3}$$

The above analysis shows that *any* system near to a point of stable equilibrium is described by this potential. Classically, we have the force $F = -V' = -m\omega^2 x$ so that Newton's equation (0.1) becomes

$$\ddot{x} + \omega^2 x = 0 \ , \tag{4.4}$$

which has general solution $x(t) = A\cos\omega t + B\sin\omega t$. A classical particle in the potential (4.3) thus oscillates around the minimum with angular frequency ω. See Figure 6.
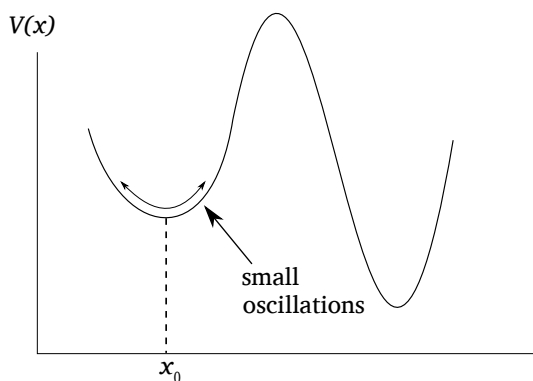

Figure 6: A particle performing small oscillations around a point of stable equilibrium of any potential $V(x)$ is described to lowest order by a harmonic oscillator.

We now turn to the corresponding quantum mechanical problem. The stationary state Schrödinger equation (2.14) of energy E is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi \ . \tag{4.5}$$

The first thing to do is to redefine variables so as to remove the various physical constants:

$$\epsilon \equiv \frac{2E}{\hbar\omega} \ , \qquad \xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \ , \tag{4.6}$$

so that (4.5) becomes

$$-\frac{\mathrm{d}^2\chi}{\mathrm{d}\xi^2} + \xi^2\chi = \epsilon\chi \ , \tag{4.7}$$

where we have defined

$$\psi(x) \equiv \chi(\xi) = \chi\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \ . \tag{4.8}$$

Although at first sight (4.7) looks like a fairly simple ODE, depending on a single constant ϵ, in fact it is not so simple to solve. However, it is not difficult to spot that $\chi(\xi) = \mathrm{e}^{\mp\xi^2/2}$ solve (4.7) with $\epsilon = \pm 1$. To see this, we compute

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\mathrm{e}^{\mp\xi^2/2}\right) = \mp\xi\,\mathrm{e}^{\mp\xi^2/2} \ , \qquad \frac{\mathrm{d}^2}{\mathrm{d}\xi^2}\left(\mathrm{e}^{\mp\xi^2/2}\right) = (\xi^2 \mp 1)\,\mathrm{e}^{\mp\xi^2/2} \ . \tag{4.9}$$

As discussed in section 3, we are only interested in *normalizable* solutions to the Schrödinger equation. For a stationary state, this means that

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x < \infty \ . \tag{4.10}$$

Via the change of variable (4.6), (4.8), for $\chi(\xi) = \mathrm{e}^{\mp \xi^2/2}$ the left hand side of (4.10) is

$$\sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} \mathrm{e}^{\mp \xi^2} \, \mathrm{d}\xi \ , \tag{4.11}$$

which is finite only for the minus sign, giving a Gaussian integral. Thus the solution $\chi(\xi) = \mathrm{e}^{+\xi^2/2}$, with $\epsilon = -1$, is *not* normalizable, and we thus discard it.

We now again change variables by defining

$$\chi(\xi) \ \equiv \ f(\xi) \, \mathrm{e}^{-\xi^2/2} \ , \tag{4.12}$$

so that

$$
\begin{aligned}
\frac{\mathrm{d}\chi}{\mathrm{d}\xi} &= \left(\frac{\mathrm{d}f}{\mathrm{d}\xi} - \xi f \right) \mathrm{e}^{-\xi^2/2} \ , \\
\frac{\mathrm{d}^2\chi}{\mathrm{d}\xi^2} &= \left[\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - \xi \frac{\mathrm{d}f}{\mathrm{d}\xi} - f - \xi \left(\frac{\mathrm{d}f}{\mathrm{d}\xi} - \xi f \right) \right] \mathrm{e}^{-\xi^2/2} \ ,
\end{aligned}
\tag{4.13}
$$

and hence (4.7) becomes

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - 2\xi \frac{\mathrm{d}f}{\mathrm{d}\xi} + (\epsilon - 1) f \ = \ 0 \ . \tag{4.14}$$

If anything, this looks worse than (4.7), so you might wonder why we bothered with (4.12)! The reasoning here is that for large values of $|\xi|$ the $\xi^2 \chi$ term in (4.7) will dominate over the $\epsilon \chi$ term; thus for large $|\xi|$ one expects solutions for different ϵ to have the same behaviour to leading order. This is why we have written $\chi(\xi)$ in (4.12) as the above normalizable $\epsilon = +1$ solution times some other function $f(\xi)$.

It is still not clear how to solve (4.14) exactly, so as usual for this type of equation we try a power series solution.[4] Thus we write

$$f(\xi) \ = \ \sum_{k=0}^{\infty} a_k \, \xi^k \ , \tag{4.15}$$

and compute

$$\xi \frac{\mathrm{d}f}{\mathrm{d}\xi} \ = \ \sum_{k=0}^{\infty} k \, a_k \, \xi^k \ , \tag{4.16}$$

and

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} \ = \ \sum_{k=0}^{\infty} (k+1)(k+2) \, a_{k+2} \, \xi^k \ . \tag{4.17}$$

---

[4] * This is a topic that could have been included in the Part A Differential Equations course, but wasn't. The point $\xi = 0$ is an *ordinary point* of (4.14), and then *Fuchs' theorem* guarantees that any solution may be expressed as a convergent Taylor series (4.15). The interested reader is referred to appendix B. Having said this, most quantum mechanics textbooks suppress these details.

Notice that the last expression involves a relabelling of the original sum. By substituting (4.15), (4.16) and (4.17) into (4.14) we obtain

$$\sum_{k=0}^{\infty} \left[(k+1)(k+2)\, a_{k+2} - 2k\, a_k + (\epsilon - 1)\, a_k \right] \xi^k \;\; = \;\; 0 \; . \tag{4.18}$$

The coefficient of every power of ξ must be separately zero, so we obtain the recurrence relation

$$a_{k+2} \;\; = \;\; \frac{2k+1-\epsilon}{(k+1)(k+2)}\, a_k \; . \tag{4.19}$$

The even and odd powers are then decoupled, giving rise to the two linearly independent series solutions

$$f_{\text{even}}(\xi) \;\; = \;\; a_0 \left[1 + \frac{(1-\epsilon)}{2!}\xi^2 + \frac{(5-\epsilon)(1-\epsilon)}{4!}\xi^4 + \cdots \right] \; ,$$
$$f_{\text{odd}}(\xi) \;\; = \;\; a_1 \left[\xi + \frac{(3-\epsilon)}{3!}\xi^3 + \frac{(7-\epsilon)(3-\epsilon)}{5!}\xi^5 + \cdots \right] \; . \tag{4.20}$$

Definition In one dimension a stationary state wave function satisfying $\psi(-x) = \pm \psi(x)$ is said to describe an $\left\{ \begin{array}{c} \text{even} \\ \text{odd} \end{array} \right\}$ parity state.

Recalling equations (4.6), (4.8) and (4.12), the total stationary state wave functions are $f_{\text{even/odd}}(\xi)\, e^{-\xi^2/2}$, which then describe even and odd parity states, respectively.

We must now determine when these solutions are normalizable. It turns out that this is the case if and only if the series in (4.20) *terminate*. We shall not provide a full, rigorous proof of this here, but instead sketch the proof. This is purely for reasons of time. A more detailed treatment may be found in the book by Hannabuss.

Notice first that either of the series in (4.20) terminating is equivalent to the statement that $f(\xi)$ is a *polynomial*, which in turn is equivalent to the statement that $a_{n+2} = 0$ for some integer $n \geq 0$, since then the recurrence relation (4.19) implies that $a_k = 0$ for all $k \geq n+2$. Note that a_0 and a_1 are necessarily non-zero, otherwise $f_{\text{even/odd}}(\xi) \equiv 0$, respectively.

Suppose that either series in (4.20) does *not* terminate. Then all the coefficients are non-zero, and the ratio

$$\frac{a_{k+2}}{a_k} \;\; \longrightarrow \;\; \frac{2}{k} \; , \qquad \text{as } k \to \infty \; . \tag{4.21}$$

Compare this asymptotic behaviour of the power series coefficients with that of the function e^{ξ^2}:

$$e^{\xi^2} \;\; = \;\; \sum_{q=0}^{\infty} \frac{1}{q!} \xi^{2q} \;\; = \;\; \sum_{k=0}^{\infty} b_k\, \xi^k \; , \tag{4.22}$$

where we have defined the coefficients

$$b_k \;\; = \;\; \left\{ \begin{array}{ll} \frac{1}{q!} \; , & k = 2q \; , \\ 0 \; , & k = 2q+1 \; . \end{array} \right. \tag{4.23}$$

For $k = 2q$ even we then have

$$\frac{b_{k+2}}{b_k} \;\; = \;\; \frac{\left(\frac{k}{2}\right)!}{\left(\frac{k+2}{2}\right)!} \;\; = \;\; \frac{2}{k+2} \;\; \longrightarrow \;\; \frac{2}{k} \; , \qquad \text{as } k \to \infty \; . \tag{4.24}$$

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Comparing to (4.21), we thus see that $f_{\text{even}}(\xi)$ and e^{ξ^2} have the same asymptotic expansion. Hence the total stationary state wave function is

$$\chi(\xi) \;=\; f(\xi)\,e^{-\xi^2/2} \;\sim\; e^{\xi^2/2} \;, \tag{4.25}$$

and thus $\psi(x) = \chi(\xi)$ is not normalizable.[5] A similar argument applies to $f_{\text{odd}}(\xi)$ and the function $\xi\,e^{\xi^2}$.

Thus for a normalizable solution the series in (4.20) must terminate. If $n \geq 0$ is the least integer for which $a_{n+2} = 0$ then the recurrence relation (4.19) implies

$$2n + 1 - \epsilon \;=\; 0 \;. \tag{4.26}$$

Recalling the definition $\epsilon = 2E/\hbar\omega$ in terms of the energy E in (4.6) then gives

$$E \;=\; E_n \;=\; \left(n + \tfrac{1}{2}\right)\hbar\omega \;. \tag{4.27}$$

The quantum harmonic oscillator energies are hence labelled by the quantum number $n \in \mathbb{Z}_{\geq 0}$; compare to (2.21) for the particle in a box (and notice there that we instead defined n so that $n \in \mathbb{Z}_{>0}$). Also note that our initial solution with $f \equiv 1$ and $\epsilon = +1$ is in fact the *ground state*, with $n = 0$. Reverting back to the original spatial coordinate x via (4.6) and (4.8), the ground state wave function is hence

$$\psi_0(x) \;=\; a_0\,e^{-m\omega x^2/2\hbar} \;, \tag{4.28}$$

where a_0 is a normalization constant, with corresponding *ground state energy* $E_0 = \tfrac{1}{2}\hbar\omega$. The normalized ground state wave function may be obtained by imposing

$$1 \;=\; |a_0|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\,\mathrm{d}x \;. \tag{4.29}$$

The Gaussian integral is that for a normal distribution of variance $\sigma^2 = \hbar/2m\omega$, and thus via the standard result for this integral we have

$$|a_0|^2 \;=\; \sqrt{\frac{m\omega}{\pi\hbar}} \;, \tag{4.30}$$

leading to the full, normalized time-dependent ground state wave function

$$\Psi_0(x,t) \;=\; \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-(m\omega x^2 + \mathrm{i}\,\hbar\omega t)/2\hbar} \;. \tag{4.31}$$

More generally the stationary state wave functions are $\chi_n(\xi) = f_n(\xi)\,e^{-\xi^2/2}$, where $f_n(\xi)$ is an even/odd polynomial in $\xi = \sqrt{\frac{m\omega}{\hbar}}\,x$ of degree n, for n even/odd, respectively. The polynomials f_n may be determined explicitly by setting $\epsilon - 1 = 2n$ in the recurrence relation (4.19). Appropriately normalized, $f_n(\xi) \equiv H_n(\xi)$ is called the *nth Hermite polynomial*. The first few polynomials are given in Table 1, with the corresponding wave functions shown in Figure 7.

Exercise Check that the polynomials in Table 1 are indeed obtained from (4.20).

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$

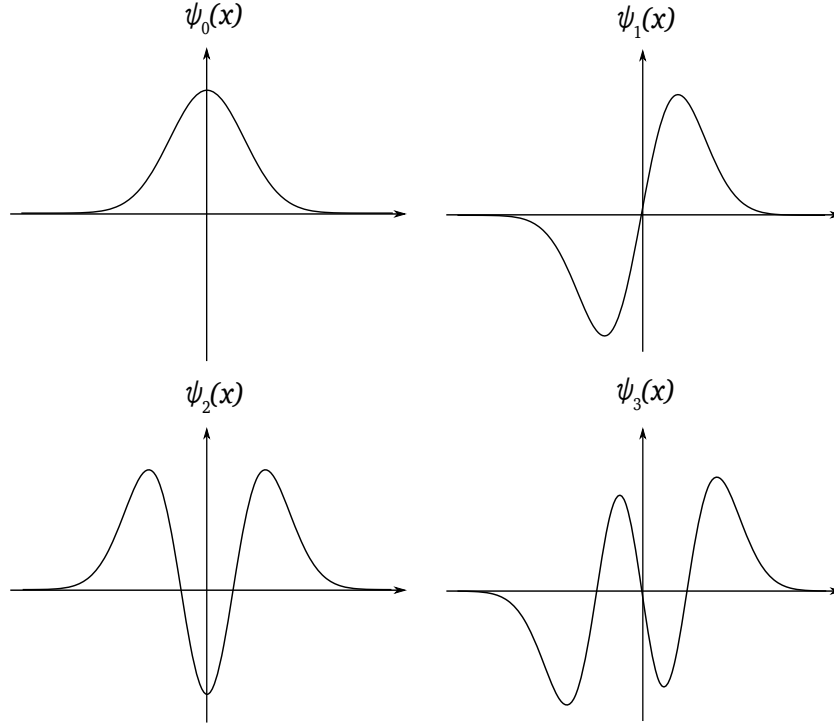Table 1: The first four Hermite polynomials.

Figure 7: The ground state and first three excited state wave functions of the harmonic oscillator.

We now summarize via

Theorem 4.1 *The energies of the one-dimensional quantum harmonic oscillator of angular frequency ω are*

$$E = E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \ ,$$

for $n \in \mathbb{Z}_{\geq 0}$ a non-negative integer. The corresponding normalized *stationary state wave functions are*

$$\psi_n(x) \;=\; \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_n(\xi)\, \mathrm{e}^{-\xi^2/2} \ , \tag{4.32}$$

where $\xi = \sqrt{m\omega/\hbar}\, x$ and H_n is the nth Hermite polynomial, defined implicitly via the generating function:

$$\exp\left(2\xi s - s^2\right) \;=\; \sum_{n=0}^{\infty} H_n(\xi)\,\frac{s^n}{n!} \ . \tag{4.33}$$

---

[5]It is the last step in (4.25) that needs a little more work to make rigorous.

Exercise (Problem Sheet 2) You'll be led through the derivation of the normalized wave functions (4.32), and the expression (4.33) for the Hermite polynomials, on the second problem sheet. Note that for $n = 0$ (4.32) agrees with the ground state result (4.31).

Let us now discuss some physics. Notice that the difference in consecutive energy levels in (4.27) is $E_{n+1} - E_n = \hbar\omega$, which is precisely the energy of a *photon* of angular frequency ω!

> * What is the relation between a quantum harmonic oscillator and a photon with the same angular frequency ω? Recall that we said the photon is massless and therefore not governed by the Schrödinger equation. While this is certainly true, it turns out that in "quantizing" the classical electromagnetic field one effectively finds an infinite set of quantum harmonic oscillators.

As stressed at the beginning of this section, the harmonic oscillator is ubiquitous in physics, and it is therefore straightforward to test these results experimentally. For example, in a diatomic molecule the two atoms perform small oscillations of some frequency ω. One can then measure the frequency of absorbed/emitted photons, finding agreement with (4.27).

As for the particle in a box, it is interesting to compare the classical and quantum harmonic oscillators. We focus here on the following new feature. In classical physics a particle of conserved energy E cannot enter a region of space where $E < V(\mathbf{r})$, as follows from the simple observation that

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \geq V(\mathbf{r}) . \tag{4.34}$$

The set $\{\mathbf{r} \in \mathbb{R}^3 \mid E < V(\mathbf{r})\}$ is called the *classically forbidden region*, for fixed particle energy E. For example, the ground state of the quantum harmonic oscillator has energy $E_0 = \frac{1}{2}\hbar\omega$, so the corresponding classically forbidden region for this energy is $\{\frac{1}{2}\hbar\omega < \frac{1}{2}m\omega^2 x^2\}$, which is the same as the set $\{|\xi| > 1\}$. The *quantum* probability of finding the particle in this region is

$$\int_{|x| > \sqrt{\hbar/m\omega}} |\Psi_0(x,t)|^2 \, dx = \frac{1}{\sqrt{\pi}} \int_{|\xi| > 1} e^{-\xi^2} \, d\xi \simeq 0.157 . \tag{4.35}$$

Here we have used (4.31) the the harmoinic oscillator ground state wave function. We thus see that there is a non-zero probability of finding the particle in a region where *classically* it is *impossible* to find the particle! This is what underlies the phenomenon of *quantum tunnelling*, although we shall not pursue this further in this course (regrettably). In keeping with the correspondence principle, for the analogous computation with energy E_n one finds the probability of finding the particle in the classically forbidden region tends to zero as $n \to \infty$. We shall not prove this though.

4.2 Higher dimensional oscillators

Having discussed the one-dimensional oscillator, it is now straightforward to extend this to oscillators in higher dimensions.

Let us begin by considering a quantum harmonic oscillator in two dimensions, with potential

$$V(x,y) = \frac{1}{2}m\left(\omega_1^2 x^2 + \omega_2^2 y^2\right) . \tag{4.36}$$

The corresponding stationary state Schrödinger equation (2.12) is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)+V(x,y)\psi \;=\; E\psi\;. \tag{4.37}$$

As for the particle in a box, this may be solved by separation of variables. One writes $\psi(x,y)=X(x)Y(y)$, so that (4.37) separates into

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2}+\frac{1}{2}m\omega_1^2 x^2 X \;=\; E_1\,X\;,$$
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 Y}{\mathrm{d}y^2}+\frac{1}{2}m\omega_2^2 y^2 Y \;=\; E_2\,Y\;, \tag{4.38}$$

where $E_1+E_2=E$. We thus have two decoupled one-dimensional oscillators, and it follows from the previous section that

$$E \;=\; E_{n_1,n_2} \;=\; \left(n_1+\tfrac{1}{2}\right)\hbar\omega_1 + \left(n_2+\tfrac{1}{2}\right)\hbar\omega_2\;, \tag{4.39}$$

where the quantum numbers $n_1, n_2 \in \mathbb{Z}_{\geq 0}$. The corresponding normalized stationary state wave functions are

$$\psi_{n_1,n_2}(x,y) \;=\; \psi_{n_1}(x)\,\psi_{n_2}(y) \tag{4.40}$$
$$=\; \frac{1}{\sqrt{2^{n_1+n_2}n_1!n_2!}}\left(\frac{m^2\omega_1\omega_2}{\pi^2\hbar^2}\right)^{1/4} H_{n_1}\left(\sqrt{\frac{m\omega_1}{\hbar}}x\right) H_{n_2}\left(\sqrt{\frac{m\omega_2}{\hbar}}y\right) \mathrm{e}^{-m(\omega_1 x^2+\omega_2 y^2)/2\hbar}\;,$$

where ψ_n denotes the normalized stationary state wave function for a one-dimensional harmonic oscillator.

Exercise Check carefully that the above statements follow from Theorem 4.1. In particular, how is the normalizable/normalized condition related to the condition in one dimension?

Of course the quadratic form appearing in (4.36) is rather special, in that it is diagonal. One can treat more general quadratic forms by first changing to *normal coordinates*, *i.e.* one first diagonalizes V by an *orthogonal transformation*. Let us illustrate with an example:

Example Consider the oscillator potential

$$V(x,y) \;=\; m\omega^2(x^2+xy+y^2) \;=\; \frac{1}{2}m\omega^2 \begin{pmatrix} x & y \end{pmatrix}\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}\;. \tag{4.41}$$

The matrix here has eigenvalues 3 and 1, so there exists an orthogonal transformation to coordinates u, v with corresponding new potential

$$\widetilde{V}(u,v) \;=\; \frac{1}{2}m\omega^2 \begin{pmatrix} u & v \end{pmatrix}\begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix}\;,$$
$$=\; \frac{1}{2}m\left(3\omega^2 u^2 + \omega^2 v^2\right)\;, \tag{4.42}$$

which is now of the form (4.36).[6] The orthogonality of the transformation ensures that the Laplacian/kinetic term in the Schrödinger equation is invariant, so

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2} \;=\; \frac{\partial^2}{\partial u^2}+\frac{\partial^2}{\partial v^2}\;. \tag{4.43}$$

---

[6]Explicitly, $u=\frac{1}{\sqrt{2}}(x+y)$, $v=\frac{1}{\sqrt{2}}(x-y)$.

Of course, since any quadratic form for V is described by a *symmetric matrix*, we may always diagonalize the potential by an orthogonal transformation, thus reducing the problem to a diagonal form for V, as in (4.36). These remarks apply in any dimension: first change to normal coordinates, then separate variables one at a time. The Schrödinger equation for *any* quadratic potential then reduces to a decoupled set of one-dimensional oscillators, so that the total energy = sum of one-dimensional energies, and the total wave functions = product of one-dimensional wave functions.

We conclude this section with another example of degenerate energy levels:

Example (Degeneracy) Consider the original two-dimensional oscillator potential (4.36) with $\omega_1 = \omega_2 = \omega$. Then

$$E \;=\; E_n \;=\; (n+1)\hbar\omega \;, \tag{4.44}$$

where $n = n_1 + n_2$. The ground state is $n_1 = n_2 = 0$, which is the unique state of energy $\hbar\omega$. However, more generally at level n there are $n + 1$ linearly independent wave functions with energy E_n, given by taking (n_1, n_2) to be $(n, 0)$, $(n-1, 1)$, ..., $(1, n-1)$, $(0, n)$. Thus E_n has degeneracy $n + 1$. Again, notice this degeneracy is related to the symmetry of the potential.

5 The hydrogen atom

5.1 Atoms

We begin with a discussion of *Coulomb's law*.[7] In general, a point charge e_2 at the origin induces an *electrostatic force* on another point charge e_1 at position $\mathbf{r}$ given by the inverse square law

$$\mathbf{F} \;=\; \frac{1}{4\pi\epsilon_0} \frac{e_1 e_2}{r^2} \frac{\mathbf{r}}{r} \;, \tag{5.1}$$

where as usual $r = |\mathbf{r}|$. Notice that the Coulomb force (5.1) is proportional to the product of the charges, so that opposite (different sign) charges attract, while like (same sign) charges repel. Electric charge is measured in *Coulombs*, C, and the proportionality constant $\epsilon_0 \simeq 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2} in (5.1) is called the *permittivity of free space*. The Coulomb force is conservative, of the form $\mathbf{F} = -\nabla V$ where

$$V(\mathbf{r}) \;=\; V(r) \;=\; \frac{1}{4\pi\epsilon_0} \frac{e_1 e_2}{r} \;, \tag{5.2}$$

is the *Coulomb potential*.

An atom consists of negatively charged electrons e^- orbiting a positively charged nucleus, where the force of attraction is (predominantly) electrostatic. An electron carries electric charge $-e$, where $e \simeq 1.60 \times 10^{-19}$ C. In general, the nucleus of an atom consists of Z positively charged protons, each of charge $+e$, and A neutrons, of charge 0, and these are tightly bound together (by the *strong force*). In the following we consider an atom of *atomic number Z*, with

---

[7] * Coulomb discovered his law in 1783. From a modern point of view, this law is subsumed into Maxwell's classical theory of electromagnetism (*i.e.* Coulomb's law can be derived from Maxwell's equations).

a *single* orbiting electron. In particular, the hydrogen atom has $Z = 1$. Since the nucleus is vastly heavier than the electron ($m_{\text{proton}} \simeq 1836\, m_{e^-}$), this implies that the centre of mass of the atomic system will always be very close to the nucleus. We thus make the simplifying assumption that the nucleus is *fixed*, at the origin. The potential for the force acting on the electron is then given by (5.2) with $e_1 = -e$, $e_2 = Ze$ (see Figure 8):

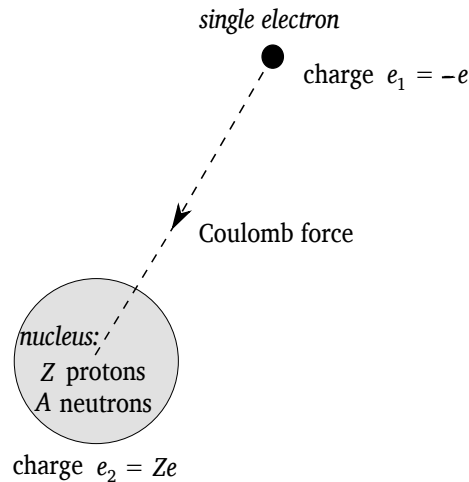$$V(r) = -\frac{Z e^2}{4\pi\epsilon_0\, r}\ . \tag{5.3}$$

Figure 8: An atom consisting of a nucleus of atomic number Z and a single orbiting electron.

Recall that in section 1.2 we discussed the empirical formula (1.4) for the energy levels of the hydrogen atom. Our task in the remainder of this course is to derive this formula theoretically, using the Schrödinger equation. However, before moving on to this, as usual we pause to make some comments on the corresponding *classical* problem. The $1/r$ Coulomb potential is formally the same as Newton's gravitational potential that you encountered in Mods, the only difference being that gravity is *always* attractive. Thus classically the atomic system in Figure 8 is similar to a planet orbiting the sun under gravity.[8] In particular, the energy levels are continuous, not discrete as in (1.4).

* There is an even more serious problem with the classical picture above. Maxwell's classical theory of electromagnetism predicts that an *accelerating* charge, such as an electron in orbit around a nucleus, emits electromagnetic radiation, and thus continuously loses energy. The electron would quickly spiral in towards the nucleus, and all atoms would hence be unstable! We shall see how quantum theory gets around this problem.

5.2 The spectrum of the hydrogen atom

We consider the three-dimensional stationary state Schrödinger equation (2.12) with potential (5.3):

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Z e^2}{4\pi\epsilon_0\, r}\,\psi = E\psi\ , \tag{5.4}$$

---

[8]Of course there is *also* a gravitational attraction between the electron and nucleus, but this is many orders of magnitude smaller.

where $m = m_{e^-} \sim 9.12 \times 10^{-31}$ kg is the mass of an electron. In this course we consider only *spherically symmetric* wave functions, so that $\psi(\mathbf{r}) = \psi(r)$ depends only on the distance r from the origin.[9] In this case, the Laplacian reduces to

$$\nabla^2 \psi \;=\; \frac{1}{r} \frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\psi) \;=\; \frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} \;, \tag{5.5}$$

and we must hence solve the ODE

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\psi) + \frac{2mZ\,e^2}{4\pi\epsilon_0\hbar^2\,r}\psi \;=\; -\frac{2mE}{\hbar^2}\psi \;. \tag{5.6}$$

Notice that by multiplying this equation by r we effectively obtain a *one-dimensional Schrödinger equation* of the form (2.14), with ψ replaced by $r\psi$ and a $1/r$ potential.

The method for solving (5.6) is very similar to that for the harmonic oscillator – there is essentially only one technical difference, as we shall see. As for the harmonic oscillator, we first change variables to remove the physical constants. We define

$$\kappa \;\equiv\; \frac{\sqrt{-2mE}}{\hbar} \;, \qquad\qquad \beta \;\equiv\; \frac{2Z}{a} \;=\; \frac{2mZ\,e^2}{4\pi\epsilon_0\hbar^2} \;, \tag{5.7}$$

where we have introduced

Definition The *Bohr radius* is

$$a \;=\; \frac{4\pi\epsilon_0\hbar^2}{me^2} \;\simeq\; 5.29 \times 10^{-11}\,\mathrm{m} \;, \tag{5.8}$$

where $m = m_{e^-}$ is the mass of the electron.

Of course, *a priori* the constant κ may be imaginary, but we are anticipating that E will be negative, as in (1.4). Equation (5.6) now becomes

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} + \frac{\beta}{r}\psi \;=\; \kappa^2\,\psi \;. \tag{5.9}$$

As for the harmonic oscillator, it turns out to be convenient to substitute

$$\psi(r) \;\equiv\; f(r)\,\mathrm{e}^{-\kappa r} \;. \tag{5.10}$$

The motivation is again similar.[10] At large values of r the term on the right hand side of (5.9) dominates over the second and third terms on the left hand side. One thus expects the $\psi(r) = A_\pm \mathrm{e}^{\pm\kappa r}$ solutions to the equation $\mathrm{d}^2\psi/\mathrm{d}r^2 = \kappa^2\psi$ to determine the leading asymptotic behaviour of solutions to (5.9). The *normalization condition* is

$$1 \;=\; \int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2\,\mathrm{d}^3x \;=\; 4\pi \int_0^\infty |\psi(r)|^2\,r^2\mathrm{d}r \;, \tag{5.11}$$

where we have taken $\psi(\mathbf{r}) = \psi(r)$, and integrated over the unit sphere of area 4π. Thus one must certainly take the minus sign in $\mathrm{e}^{\pm\kappa r}$ to obtain a normalizable solution near to $r = \infty$.

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[9]The more general case is studied in the third year course.

[10]The argument in the following paragraph is again really a sketch, rather than a rigorous treament. It is in any case simply a justification for the substitution (5.10).

We also see that E must be *negative*; otherwise $|e^{\pm\kappa r}| = 1$, and this asymptotic solution is not normalizable at infinity.

The substitution (5.10) leads to

$$\frac{d\psi}{dr} = \left(\frac{df}{dr} - \kappa f\right) e^{-\kappa r},$$

$$\frac{d^2\psi}{dr^2} = \left(\frac{d^2 f}{dr^2} - 2\kappa \frac{df}{dr} + \kappa^2 f\right) e^{-\kappa r}, \tag{5.12}$$

so that (5.9) becomes

$$\frac{d^2 f}{dr^2} + \frac{2}{r}(1 - \kappa r)\frac{df}{dr} + \frac{1}{r}(\beta - 2\kappa)f = 0. \tag{5.13}$$

We again try a series solution. The main technical difference with the harmonic oscillator equation is that the coefficients in (5.13) are *singular* at $r = 0$.[11] Thus *a priori* we should write

$$f(r) = \sum_{k=0}^{\infty} a_k r^{k+c}, \tag{5.14}$$

for some real constant $c \in \mathbb{R}$. Without loss of generality, we may assume $a_0 \neq 0$. We then have

$$\frac{df}{dr} = \sum_{k=0}^{\infty}(k + c) a_k r^{k+c-1},$$

$$\frac{d^2 f}{dr^2} = \sum_{k=0}^{\infty}(k + c)(k + c - 1) a_k r^{k+c-2}. \tag{5.15}$$

Thus (5.13) becomes

$$\sum_{k=0}^{\infty} \Big\{(k + c)(k + c - 1) a_k + 2[(k + c) a_k - \kappa(k + c - 1) a_{k-1}]$$
$$+ (\beta - 2\kappa) a_{k-1}\Big\} r^{k+c-2} = 0, \tag{5.16}$$

where we define $a_{-1} = 0$. The *lowest* power of r in (5.16) is r^{c-2}, with coefficient

$$a_0 \left[c(c - 1) + 2c\right] = 0. \tag{5.17}$$

Since $a_0 \neq 0$, we thus have

$$c(c - 1) + 2c = 0 \quad \Rightarrow \quad c(c + 1) = 0 \quad \Rightarrow \quad c = 0 \quad \text{or} \quad c = -1. \tag{5.18}$$

However, if $c = -1$ then from (5.14) the wave function $\psi(r) = f(r) e^{-\kappa r} \sim \frac{a_0}{r}$ near to $r = 0$. The wave function is *singular* at the origin with this choice of c, and we thus discard this solution. Hence $c = 0$, and the recurrence relation derived from the coefficient of r^{k-2} in (5.16) simplifies to

$$k(k - 1) a_k + 2[k a_k - \kappa(k - 1) a_{k-1}] + (\beta - 2\kappa) a_{k-1} = 0, \tag{5.19}$$

---

[11] * More precisely, $r = 0$ is a *regular singular point* of (5.13). Again, Fuchs' theorem applies and determines the form of the series in (5.14). See appendix B.

or, after some cancellations, equivalently

$$a_k = \frac{2\kappa k - \beta}{k(k+1)} a_{k-1} \ . \tag{5.20}$$

The solution is hence

$$f(r) = a_0 \left[1 + \frac{(2\kappa - \beta)}{2} r + \frac{(4\kappa - \beta)(2\kappa - \beta)}{12} r^2 + \cdots \right] \ . \tag{5.21}$$

Notice that, in contrast to the harmonic oscillator, here we have only a *single* solution – we have already discarded the $c = -1$ solution as singular and thus unphysical.

Finally, we must impose that the wave function resulting from (5.21) is normalizable. Suppose that the series does *not* terminate. Then

$$\frac{a_k}{a_{k-1}} \longrightarrow \frac{2\kappa}{k} \ , \qquad \text{as } k \to \infty \ . \tag{5.22}$$

Compare this to the Taylor expansion of the function $e^{2\kappa r} = \sum_{k=0}^{\infty} b_k \, r^k$, where $b_k = (2\kappa)^k/k!$. In this case

$$\frac{b_k}{b_{k-1}} = \frac{(2\kappa)^k \, (k-1)!}{(2\kappa)^{k-1} \, k!} = \frac{2\kappa}{k} \ . \tag{5.23}$$

Thus if the series (5.21) does not terminate the function $f(r)$ and $e^{2\kappa r}$ have the same asymptotic expansion, and hence

$$\psi(r) = f(r) \, e^{-\kappa r} \sim e^{\kappa r} \tag{5.24}$$

is *not* normalizable in (5.11).

The series must hence terminate; that is, there is a least integer $n > 0$ such that $a_n = 0$. The recurrence relation (5.20) then gives

$$2\kappa n - \beta = 0 \ . \tag{5.25}$$

Recalling the definitions (5.7) of κ and β, this becomes

$$E = -\frac{\hbar^2}{2m} \kappa^2 = -\frac{\hbar^2}{2m} \cdot \frac{Z^2}{a^2 \, n^2} \ , \tag{5.26}$$

so that

$$E = E_n = -\frac{Z^2 \, \hbar^2}{2ma^2} \cdot \frac{1}{n^2} \ , \tag{5.27}$$

which is precisely of the form (1.4)! Moreover, we have a theoretical formula for the Rydberg constant, namely (putting $Z = 1$ for hydrogen)

$$R_0 = \frac{\hbar}{4\pi \, mca^2} = \frac{me^4}{(4\pi)^3 \, \epsilon_0^2 \, \hbar^3 c} \ , \tag{5.28}$$

where m is the electron mass, c is the speed of light, and a is the Bohr radius.

In general $f(r) = f_n(r)$ is a polynomial of degree $n-1$. In particular, the *ground state* has $n = 1$ with $f(r) = a_0$ a constant. The corresponding ground state wave function is

$$\psi_1(r) = a_0 \, e^{-\kappa_1 r} = a_0 \, e^{-Zr/a} \ , \tag{5.29}$$

where we have used (5.25) to write $\kappa = \kappa_n = \beta/2n = Z/an$. It is straightforward to normalize (5.29) using (5.11):

$$
\begin{aligned}
1 & = 4\pi \, |a_0|^2 \int_0^\infty r^2 \, \mathrm{e}^{-2\kappa_1 r} \, \mathrm{d}r \;, \\
& = \pi \, |a_0|^2 \, \frac{\mathrm{d}^2}{\mathrm{d}\kappa_1^2} \int_0^\infty \mathrm{e}^{-2\kappa_1 r} \, \mathrm{d}r \;, \\
& = \pi \, |a_0|^2 \, \frac{\mathrm{d}^2}{\mathrm{d}\kappa_1^2} \left[\frac{1}{2\kappa_1} \right] \;, \\
& = \frac{\pi \, |a_0|^2 \, a^3}{Z^3} \;,
\end{aligned}
\tag{5.30}
$$

thus giving $a_0 = \sqrt{Z^3/\pi \, a^3}$ and hence

$$
\psi_1(r) \;=\; \sqrt{\frac{Z^3}{\pi \, a^3}} \, \mathrm{e}^{-Zr/a} \;,
\tag{5.31}
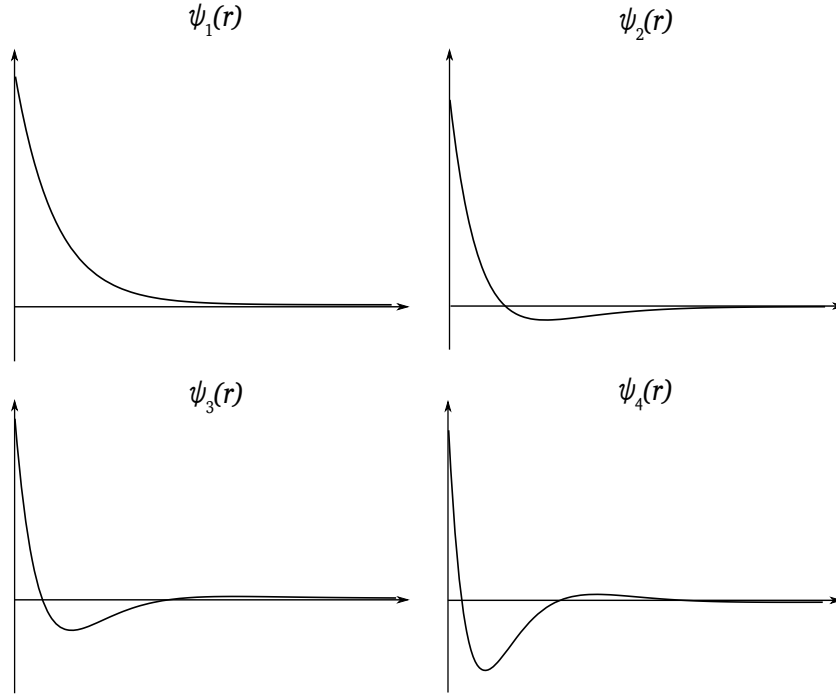$$

is the *normalized ground state wave function.*

Figure 9: The ground state and first three excited state wave functions of the (spherically symmetric) hydrogen atom.

More generally, the polynomials f_n, appropriately normalized, are called *generalized Laguerre polynomials*. More specifically,

$$
f_n(r) \;=\; L_{n-1}^1 \left(\frac{2Zr}{an} \right) \;=\; L_{n-1}^1 \left(2\kappa_n r \right) \;,
\tag{5.32}
$$

where the first few polynomials $L_{n-1}^1(s)$ are shown in Table 2.

Exercise Check that the polynomials in Table 2 are indeed obtained from (5.21).

n	$L^1_{n-1}(s)$
1	1
2	$-s + 2$
3	$\frac{s^2}{2} - 3s + 3$
4	$-\frac{s^3}{6} + 2s^2 - 6s + 4$

Table 2: The generalized Laguerre polynomials that determine the ground state and first three excited states of the (spherically symmetric) hydrogen atom.

* The generalized Laguerre polynomials may be defined via

$$L^\alpha_N \;\; \equiv \;\; \frac{s^{-\alpha}\,\mathrm{e}^s}{N!}\,\frac{\mathrm{d}^N}{\mathrm{d}s^N}\left(s^{N+\alpha}\,\mathrm{e}^{-s}\right)\;. \tag{5.33}$$

This is a polynomial of degree N. Our case above is $N = n - 1$, $\alpha = 1$, although we shall not prove that (5.33) follows from (5.21) here. Related to this, you might wonder how general the spherically symmetric case is. Allowing $\psi = \psi(r, \theta, \phi)$ in (5.4) one finds that the spectrum of energies (5.27) is the *same*, but now E_n has *degeneracy n^2*. The general wave functions involve *spherical harmonics* and the more general Laguerre polynomials in (5.33), with $\alpha \geq 1$. The proof of these facts is in the third year quantum course.

We summarize with

Theorem 5.1 *The (spherically symmetric) energy levels for an atom consisting of a single electron orbiting a nucleus of atomic number Z are*

$$E \;\; = \;\; E_n \;\; = \;\; -\frac{Z^2\,\hbar^2}{2ma^2}\cdot\frac{1}{n^2}\;, \tag{5.34}$$

where the positive integer n is called the principal quantum number. *The corresponding spherically symmetric wave functions are*

$$\psi_n(r) \;\; = \;\; C_n\,L^1_{n-1}\left(\frac{2Zr}{an}\right)\mathrm{e}^{-Zr/an}\;, \tag{5.35}$$

where C_n are appropriate normalization constants and L^1_{n-1} is a polynomial of degree $n - 1$.

In particular, the normalized ground state wave function is

$$\psi_1(r) \;\; = \;\; \sqrt{\frac{Z^3}{\pi\,a^3}}\,\mathrm{e}^{-Zr/a}\;. \tag{5.36}$$

Notice that there is a *minimum energy* ground state, with $n = 1$, which leads to a *stable atom*. We conclude with an example computation using the hydrogen atom ground state wave function (5.36):

Example Let us compute the expectation value of r, the distance of the electron from the

nucleus, in the ground state. This is given by

$$\begin{aligned}
\langle r \rangle_{\psi_1} &= \int_0^\infty r \, |\psi_1(r)|^2 \, 4\pi r^2 \, \mathrm{d}r \ , \\
&= -\frac{4\pi a_0^2}{8} \frac{\mathrm{d}^3}{\mathrm{d}\kappa_1^3} \left[\frac{1}{2\kappa_1} \right] \ , \\
&= \frac{3\pi a_0^2}{2\kappa_1^4} \ , \\
&= \frac{3a}{2Z} \ ,
\end{aligned}$$

(5.37)

where we have used $a_0 = \sqrt{Z^3/\pi \, a^3}$ in (5.29). Thus for the hydrogen atom, with $Z = 1$, the average distance of the electron from the nucleus, in the ground state, is $\frac{3}{2}$ times the Bohr radius a, which numerically is $\simeq 7.94 \times 10^{-11}$ m.

A Summary: vectors and vector operators

The following summarizes some basic notation and conventions used in the main text.

We work in $\mathbb{R}^3$, or a domain therein, in Cartesian coordinates. If $\mathbf{e}_1 = \mathbf{i} = (1,0,0)$, $\mathbf{e}_2 = \mathbf{j} = (0,1,0)$, $\mathbf{e}_3 = \mathbf{k} = (0,0,1)$ denote the standard orthonormal basis vectors, then a position vector is

$$\mathbf{r} = \sum_{i=1}^3 x_i \, \mathbf{e}_i \ ,$$

(A.1)

where $x_1 = x$, $x_2 = y$, $x_3 = z$ are the Cartesian coordinates in this basis. The *scalar product* of two vectors $\mathbf{a}$, $\mathbf{b}$ is denoted by

$$\mathbf{a} \cdot \mathbf{b} = \sum_{i=1}^3 a_i b_i \ .$$

(A.2)

We denote the Euclidean length of $\mathbf{r}$ by

$$|\mathbf{r}| = r = \sqrt{x_1^2 + x_2^2 + x_3^2} = \sqrt{\mathbf{r} \cdot \mathbf{r}} \ .$$

(A.3)

The *gradient* of a function $\phi = \phi(\mathbf{r})$ is the vector field

$$\mathbf{grad} \, \phi = \nabla \phi = \sum_{i=1}^3 \frac{\partial \phi}{\partial x_i} \, \mathbf{e}_i \ .$$

(A.4)

The *divergence* of a vector field $\mathbf{f} = \mathbf{f}(\mathbf{r})$ is the function (scalar field)

$$\mathrm{div} \, \mathbf{f} = \nabla \cdot \mathbf{f} = \sum_{i=1}^3 \mathbf{e}_i \cdot \frac{\partial \mathbf{f}}{\partial x_i} = \sum_{i=1}^3 \frac{\partial f_i}{\partial x_i} \ .$$

(A.5)

The second order operator ∇^2 defined by

$$\nabla^2 \phi = \nabla \cdot (\nabla \phi) = \sum_{i=1}^3 \frac{\partial^2 \phi}{\partial x_i^2}$$

(A.6)

is called the *Laplacian*.

We also remind the reader of

Theorem A.1 *(Divergence Theorem) Let D be a bounded region in $\mathbb{R}^3$ with boundary surface $S = \partial R$. If $\mathbf{f}$ is a vector field then*

$$\int_D \nabla \cdot \mathbf{f} \, \mathrm{d}^3 x \;\; = \;\; \int_S \mathbf{f} \cdot \mathbf{n} \, \mathrm{d}S \tag{A.7}$$

where $\mathbf{n}$ is the outward *unit normal vector to $S = \partial R$. One sometimes writes $\mathrm{d}\mathbf{S} \equiv \mathbf{n}\, \mathrm{d}S$.*

B * Fuchs' theorem and Frobenius series

This appendix is included only for interest and completeness. It is certainly not intended to be part of the course.

In the main text we solved both the harmonic oscillator (4.14) and spherically symmetric hydrogen atom (5.13) ODEs using a (generalized) power series expansion. Here we discuss this problem more generally. Consider the second order ODE

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + p(x)\frac{\mathrm{d}f}{\mathrm{d}x} + q(x)\, f \;\; = \;\; 0 \;, \tag{B.1}$$

for the function $f(x)$. A point x_0 is called an *ordinary point* of (B.1) if $p(x)$, $q(x)$ have Taylor expansions about x_0, valid in some positive radius of convergence; otherwise x_0 is called a *singular point*. If x_0 is a singular point, but $(x - x_0)p(x)$, $(x - x_0)^2 q(x)$ both have Taylor expansions around x_0, then x_0 is called a *regular singular point.*

By a *generalized power series*, or *Frobenius series*, about x_0 we mean

$$f(x) \;\; = \;\; \sum_{k=0}^{\infty} a_k \, (x - x_0)^{k+c} \;, \tag{B.2}$$

for some real number $c \in \mathbb{R}$. Without loss of generality, $a_0 \neq 0$. Notice that for c a non-negative integer this reduces to a normal power series. Without loss of generality, we now set $x_0 = 0$. The equation obtained from the ODE (B.1) by setting the *lowest power* of x to zero in the expansion (B.2) is called the *indicial equation*. Since (B.1) is second order, this is a quadratic equation for c. Fuchs and Frobenius proved the following result:

Theorem B.1

- If $x = 0$ *is an ordinary point, then (B.1) possesses two distinct power series solutions, so that one can effectively set $c = 0$ in (B.2). These series converge for $|x| < r$, where r is the minimum radius of convergence of $p(x)$ and $q(x)$.*

- If $x = 0$ *is a regular singular point, then there is* at least one *solution of (B.1) of the form (B.2). Again, this series solution converges for $|x| < r$, where r is the minimum radius of convergence of $xp(x)$ and $x^2 q(x)$.*

The precise behaviour for regular singular points is a little involved. If the indicial equation for c has *distinct* roots that differ by a *non-integer*, then there are *two* series solutions of the form (B.2), with the corresponding values of c solving the indicial equation. Otherwise there is not *necessarily* a second series solution; if there is not one can nevertheless say more about the second solution, but we refer the interested reader to the literature for details.